

Advances in
**ORGANOMETALLIC
CHEMISTRY**
VOLUME 41



ACADEMIC PRESS

Advances in
ORGANOMETALLIC CHEMISTRY

VOLUME 41

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Advances in Organometallic Chemistry

EDITED BY

F. GORDON A. STONE

DEPARTMENT OF CHEMISTRY
BAYLOR UNIVERSITY
WACO, TEXAS

ROBERT WEST

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

VOLUME 41



ACADEMIC PRESS

San Diego London Boston New York
Sydney Tokyo Toronto

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0065-3055/97 \$25.00

Academic Press

a division of Harcourt Brace & Company

525 B Street, Suite 1900, San Diego, California 92101-4495, USA

<http://www.apnet.com>

Academic Press Limited

24-28 Oval Road, London NW1 7DX, UK

<http://www.hbuk.co.uk/ap/>

International Standard Book Number: 0-12-031141-0

PRINTED IN THE UNITED STATES OF AMERICA

97 98 99 00 01 02 QW 9 8 7 6 5 4 3 2 1

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Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

RUDOLF AUMANN (165), Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität, 48149 Münster, Germany

KEVIN P. GABLE (127), Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

PRADEEP MATHUR (243), Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076, India

HUBERT NIENABER (165), Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität, 48149 Münster, Germany

LOTHAR WEBER (1), Fakultät für Chemie der Universität Bielefeld, D-33615 Bielefeld, Germany

MICHAEL J. WENT (69), Department of Chemistry, University of Kent, Canterbury, Kent CT2 7NH, United Kingdom

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Transition-Metal Assisted Syntheses of Rings and Cages from Phosphaalkenes and Phosphaalkynes

LOTHAR WEBER

*Fakultät für Chemie der Universität Bielefeld
D-33615 Bielefeld, Germany*

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I

INTRODUCTION

For a long time, molecules exhibiting multiple bonding to phosphorus and its heavier congeners were considered to be nonexistent. This impression, mainly gained from unsuccessful efforts to synthesize stable compounds with $P=C$ - and $P\equiv C$ - bonds, was given a theoretical rationale by the so-called double-bond rule, which for thermodynamic reasons (poor $p_{\pi}-p_{\pi}$ overlap, large interatomic distances, etc.) excluded such functionalities in stable organophosphorus molecules.¹

Within only three decades, isolable phosphaalkenes ($R^1P=CR^2R^3$) and phosphaalkynes ($R-C\equiv P$) passed from nonexistent species to laboratory curiosities, and on to becoming valuable and versatile building blocks in organic, inorganic, and organometallic chemistry. This development has been summarized in a series of reviews.^{2,3} A number of transformations with PC-multiple bond systems, which afforded ring and cage compounds,

are accomplished by the assistance of transition-metal centers. The role of the metal in these reactions is diverse. Thus, a well-defined metal complex featuring a phosphalkene or -alkyne ligand may serve as a precursor. In other cases metal complexes may be involved as reactive intermediates with the transition-metal–ligand fragment serving as a template. Reactions of phosphalkenes with transition-metal–ligand moieties directly connected to the PC skeleton, or alternatively in the periphery of the organophosphorus molecule, need also to be considered. This article gives an account of transition-metal-assisted syntheses of organophosphorus rings and cages involving phosphalkenes and phosphalkynes as precursors. The scope of this review also includes those ring and cage syntheses where the metal has not been removed from the resulting product. The review is divided into two parts, dealing with phosphorus–carbon double and triple bond systems, respectively.

II

PHOSPHAALKENES AS LIGANDS IN TRANSITION-METAL COMPLEXES

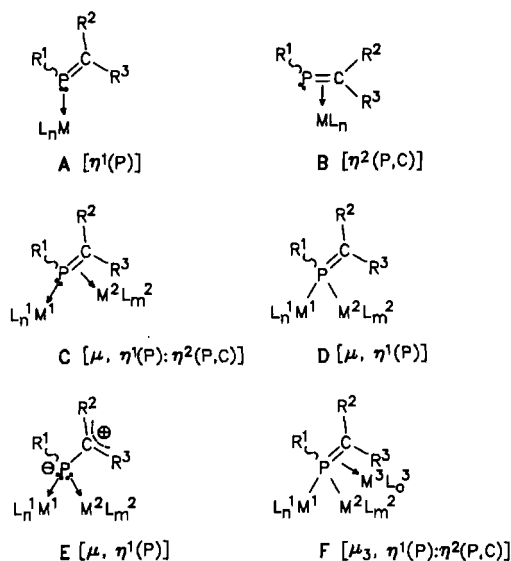
Phosphalkenes act as versatile donors in transition-metal chemistry by virtue of the filled high-lying nonbonding orbital at phosphorus containing the lone pair and/or via the $P=C$ π -bond. Moreover, back-bonding of electron-density from the metal to the organophosphorus ligand is conceivable by means of a low-lying $P=C$ π^* orbital. There are six different types (**A–F**) of complex so far known containing phosphalkene ligands.³ (See Scheme 1.) The structural integrity of the phosphalkene ligand is largely retained in the complexes of type **A–F**. In metallophosphalkenes, on the other hand, one or more of the substituents R of a given phosphalkene are replaced by transition-metal complex fragments, so that five basically different types of structure **G–K** can be differentiated.⁴ (See Scheme 2.) In principle, the lone pair of electrons as well as the $P=C$ π -bond in **G–K** may also be involved in coordinative interactions with additional metal centers. 1-Metallo-1,2-diphospha-2-propenes of the type **L** are also useful starting materials for the synthesis of organophosphorus ring compounds.

III

RINGS AND CAGES FROM PHOSPHAALKENES

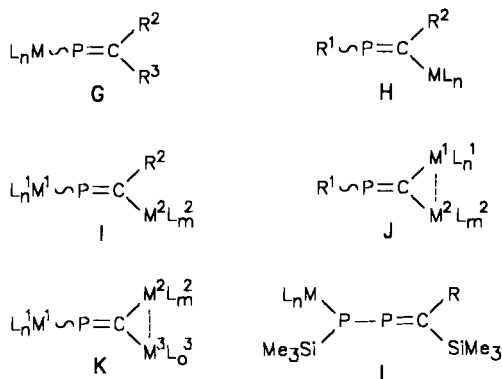
A. Three-Membered Rings

Basically, three-membered phosphorus heterocycles should result from $[2+1]$ -cycloadditions involving phosphalkenes and carbenes, carbenoids,

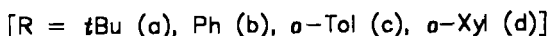


SCHEME 1.

or equivalents thereof. In keeping with this, the metallophosphaalkene **1** smoothly adds isocyanides to give the 2-imino-1-metallo-1-phosphiranes **2a–d**. No efforts are made to remove the transition-metal-complex fragment from the resulting heterocycles; see Eq. (1).⁵

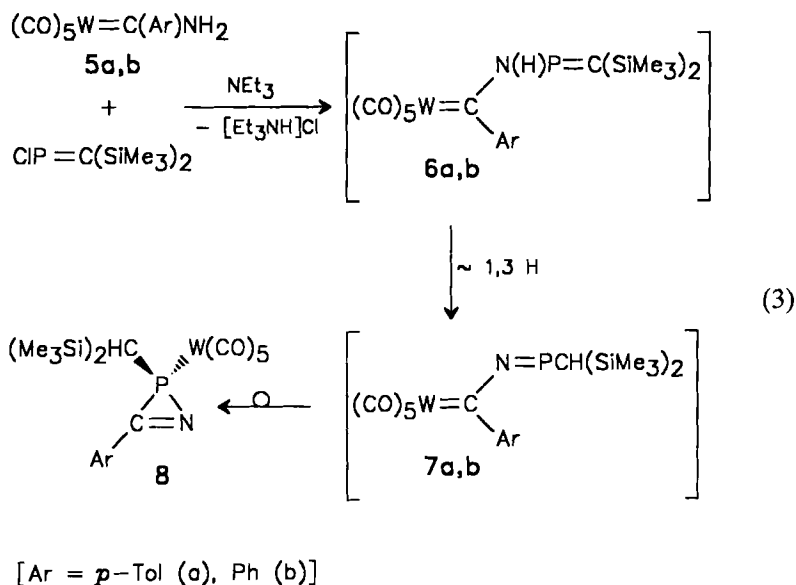


SCHEME 2.

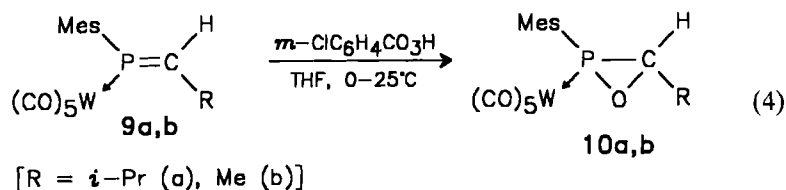


$$\begin{array}{c}
 \text{O} \\
 | \\
 \text{OC}-\text{Fe}-\text{P}=\text{C}-\text{SiMe}_3 \\
 | \quad | \\
 \text{OC} \quad \text{OC} \\
 \text{3}
 \end{array}
 \xrightarrow[\text{- C}_3\text{H}_4]{\text{THF, -30}^\circ\text{C, 30min}}
 \begin{array}{c}
 \text{(CO)}_3 \\
 | \\
 \text{Fe} \\
 | \\
 \text{Fe} \\
 | \\
 \text{(CO)}_3 \\
 \text{P} \quad \text{P}=\text{C}-\text{SiMe}_3 \\
 | \quad | \\
 \text{Me}_3\text{Si} \quad \text{SiMe}_3 \\
 \text{4}
 \end{array}
 \quad (2)$$

The first 2*H*-1-aza-2-phosphirene complexes **8a,b** result from the action of amino-carbene complexes **5a,b** with $\text{ClP}=\text{C}(\text{SiMe}_3)_2$ in the presence of triethylamine. A rationale for the products **8a,b** invokes the initial formation of carbene complex-functionalized phosphalkenes **6a,b**, which undergo 1,3-hydrogen shifts and isomerization of the transient iminophosphanes **7a,b**. Intermediates, however, are not detectable; see Eq. (3).⁷

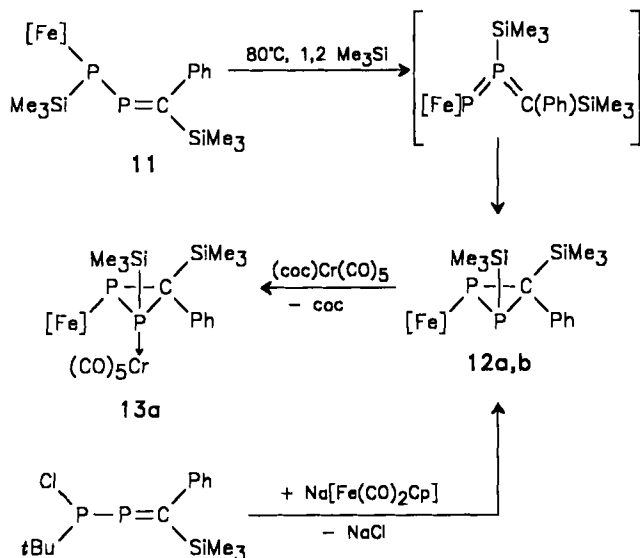


Oxaphosphiranes are interesting as they are analogs of the well-known oxiranes (epoxides). The direct epoxidation of free phosphalkenes most likely would be complicated or thwarted by oxygen attack at phosphorus. An elegant route to oxaphosphirane complexes **10a,b** makes use of the quantitative oxidation of η^1 -phosphaalkene complexes **9a,b** with *m*-chloroperbenzoic acid in THF; see Eq. (4).⁸



The thermolysis of 1-ferrio-1,2-diphosphapropene **11** in methylcyclohexane solution at 80°C affords 1-metallodiphosphirane **12a**, which is conveniently converted into its $[\text{Cr}(\text{CO})_5]$ -adduct **13a** by treatment with $[(Z)\text{-cyclooctene}]\text{Cr}(\text{CO})_5$ (Scheme 3).⁹ Similarly, 1,2-diphosphapropene $t\text{-Bu}(\text{Cl})\text{P}=\text{P}=\text{C}(\text{Ph})\text{SiMe}_3$ and $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$ afford the diphosphirane **12b** (Scheme 3).¹⁰ Trimethylsilyl group migrations from the metalated phosphorus atom to the α -position with concomitant cyclization provide a mechanistic explanation for generation of the ring. This synthetic approach can be extended to PH-functionalized 1-metallodiphosphiranes, as evidenced by the base-assisted condensation of the phosphido complex $\text{Cp}^*(\text{CO})_2\text{FePH}_2$ with $\text{ClP}=\text{C}(\text{SiMe}_3)_2$ to yield **12c** and its $[(\text{CO})_5\text{Cr}]$ derivative **13c**, respectively (Scheme 4).¹¹

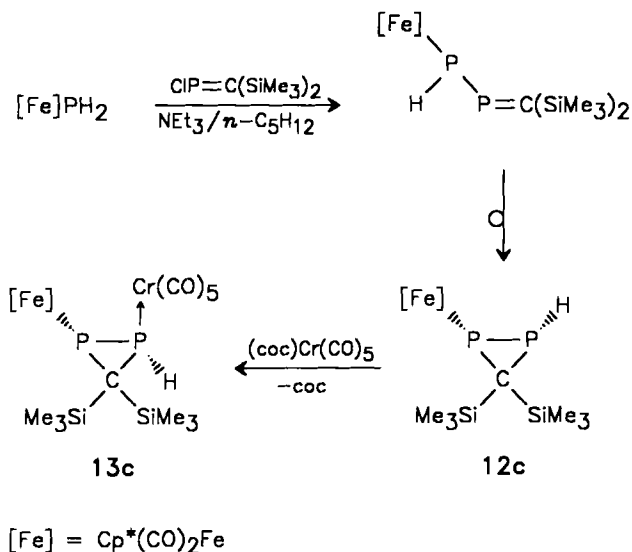
The course of this reaction is sensitively controlled by the nature of the substituents at the cyclopentadienyl ring, as well as at the phosphorus and the methylene carbon atoms. Thus, warming toluene solutions of the 1-ferriodiphosphapropenes **14a** or **14b** leads to the formation of the 1,2-



$[[\text{Fe}]] = \text{Cp}^*(\text{CO})_2\text{Fe}$ (a), $\text{Cp}(\text{CO})_2\text{Fe}$ (b)]

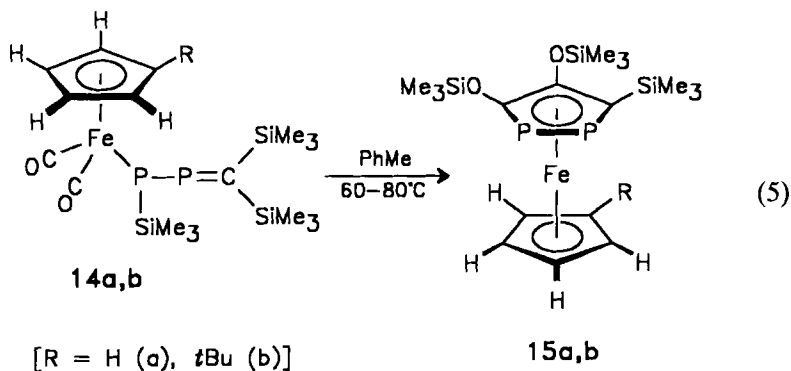
[coc = (Z)-cyclooctene]

SCHEME 3.



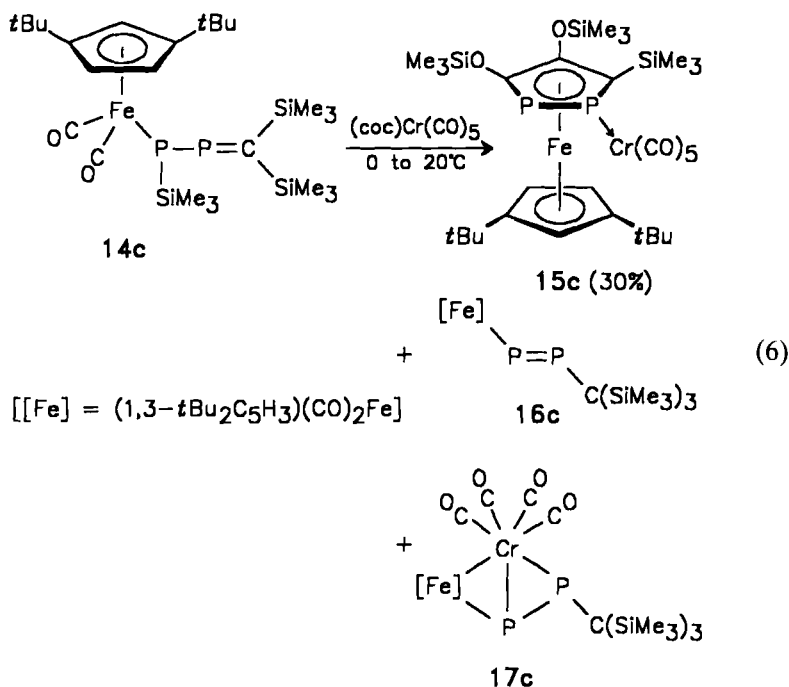
SCHEME 4.

diphosphaferrocenes **15a,b**. No diphosphiranes are detected in these transformations; see Eq. (5).^{12,13}

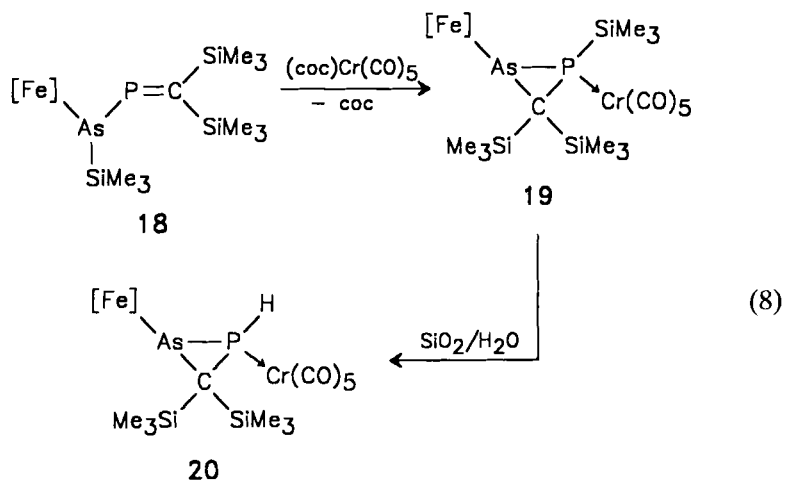
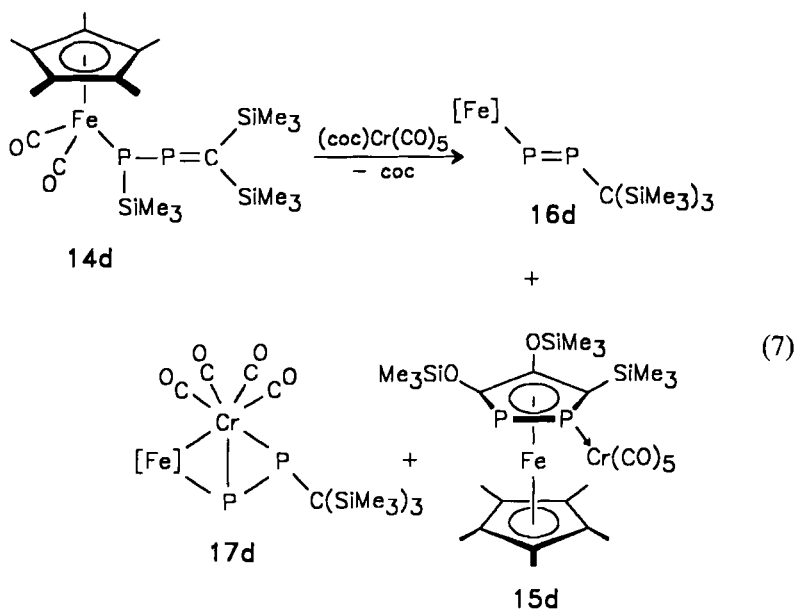


1-Ferrio-1,2-diphosphapropene **14c**, featuring an increased steric demand at the cyclopentadienyl ligand, decomposes under similar conditions. Re-

arrangement to 1,2-diphosphaferrocene **15c**, however, is effected when the compound is treated with [(*Z*)-cyclooctene]Cr(CO)₅. Minor products of this process are the metallodiphosphene **16c** and its [(CO)₄Cr] derivative **17c**, as shown in Eq. (6).¹⁴

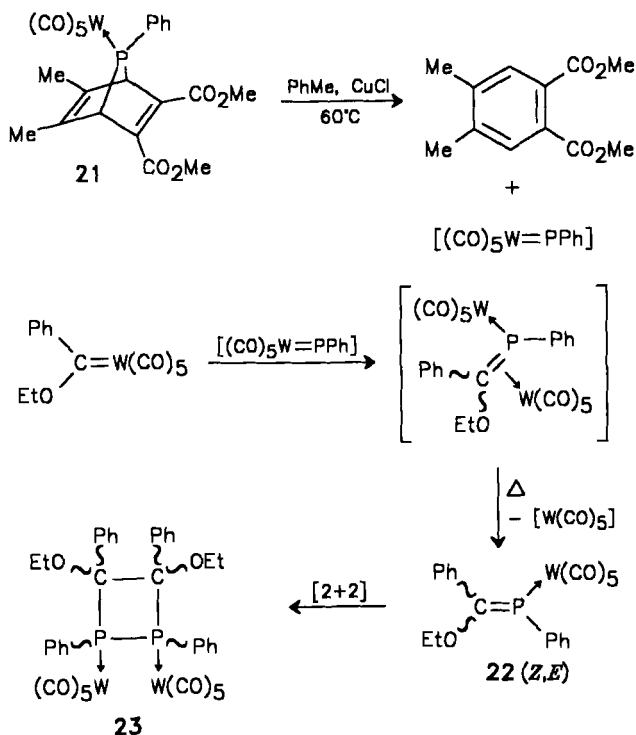


Further increase in the steric bulk of the cyclopentadienyl ring, as occurs in **14d**, leads to a situation where reaction of the metallodiphosphapropene with the carbonylchromium reagents affords $\text{Cp}^*(\text{CO})_2\text{FeP}=\text{PC}(\text{SiMe}_3)_3$ (**16d**) and its tetracarbonylchromium complex **17d** as the principal products. Only a few crystals of the 1,2-diphosphaferrocene **15d** are obtained; see Eq. (7).¹⁵ In contrast, 1-ferrio-1-arsa-2-phosphapropene (**18**) and [(*Z*)-cyclooctene]Cr(CO)₅ afford 1-ferrio-2-phosphaarsirane (**19**), which upon chromatography is converted into the corresponding PH derivative **20**; see Eq. (8).¹⁶

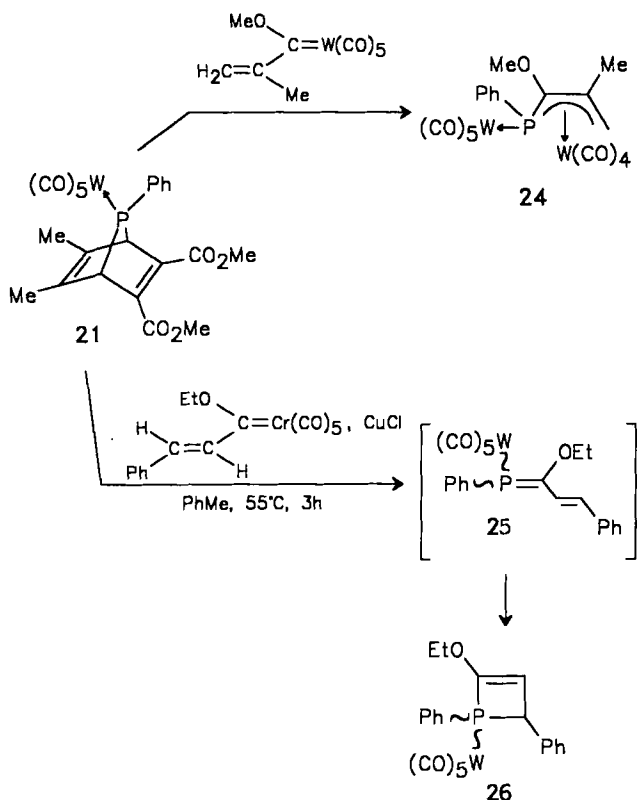


B. Four-Membered Rings

The condensation of the transient phosphinidene species $[(\text{CO})_5\text{W}=\text{PPh}]$ with carbene complexes constitutes a valuable synthetic approach to carbonylmetal complexes of phosphaaalkenes such as **22**. If the transformation, according to Scheme 5, is performed with a high dilution of reagents, the phosphaaalkene complexes are isolated as oils. Heating a concentrated toluene solution of **22** in the presence of CuCl leads to clean dimerization yielding the corresponding 1,2-diphosphetane complex **23**. In keeping with this, highly concentrated solutions of carbene complex and phosphanorbornadiene **21** directly afford the four-membered heterocycle. In the first step of this reaction sequence, the copper(I) chloride has the role of a catalyst promoting the decomposition of the phosphinidene precursor **21**, and does not interfere with the phosphinidene-carbene coupling itself (Scheme 5).^{17,18} Generation of the dinuclear η^4 -phospha-



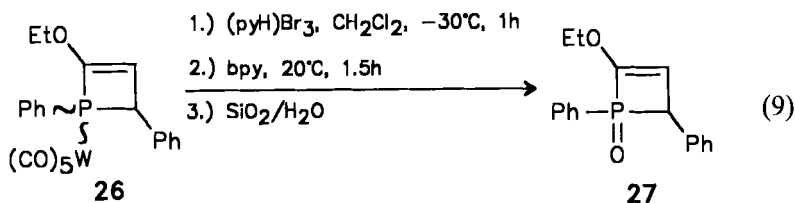
SCHEME 5.



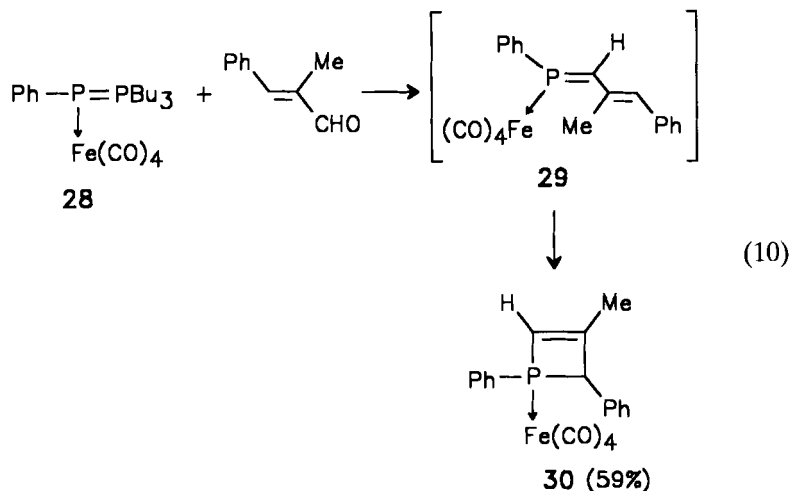
SCHEME 6.

tadiene complex **24** occurs when **21** reacts with a tungsten–vinylcarbene complex (Scheme 6).¹⁹ The employment of a chromium–vinylcarbene complex reaction with **21** affords the η^1 -1-phosphabutadiene complex **25** as a transient species, which undergoes rapid cyclization to the 1,2-dihydrophosphete **26**. An explanation for this result is based upon the observation that η^2 - $\text{P}=\text{C}$ chromium complexes are more labile than their tungsten analogs.¹⁸

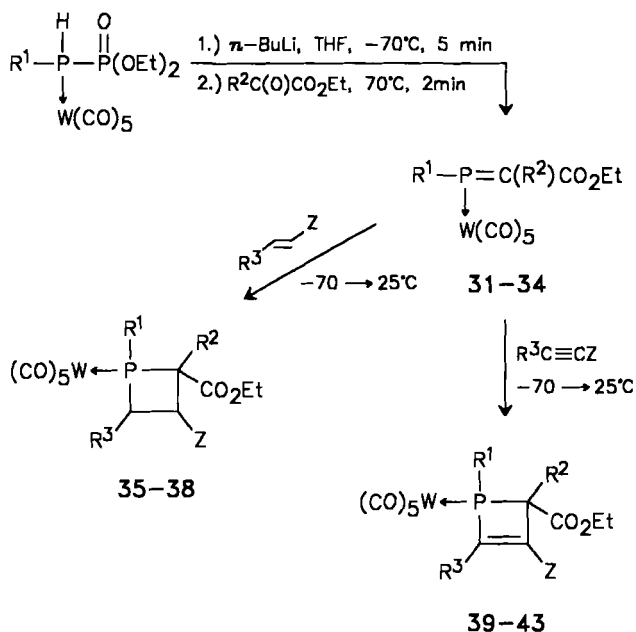
Decomplexation of the phosphorus atom of **26** and conversion into the stable 1,2-dihydrophosphete *P*-oxide **27** is achieved by successive treatment with pyridinium tribromide, 2,2'-bipyridyl, followed by a chromatographic workup; see Eq. (9).¹⁹



The phospha-Wittig reaction between $[\text{W}(\text{CO})_5]$ adducts of phosphinidene phosphoranes or phosphoranyl phosphides and organocarbonyl compounds provides an elegant complementary route to reactive phosphaaalkene complexes.^{20–23} Accordingly, **28** converts an α,β unsaturated aldehyde into a transient 1-phosphabutadiene complex **29**, which instantaneously cyclizes to **30**, as shown in Eq. (10).²³



One of the classic approaches toward cyclobutanes and cyclobutenes, [2+2] cycloaddition between electron-rich and electron-poor alkenes or alkynes, is mirrored by the *in situ* reaction of $[\text{W}(\text{CO})_5]$ adducts of electron-deficient phosphaaalkenes with enamines, enol ethers, ynamines, and ethoxyacetylene to yield the corresponding phosphetanes and 1,2-dihydrophosphetes.²¹ Prior



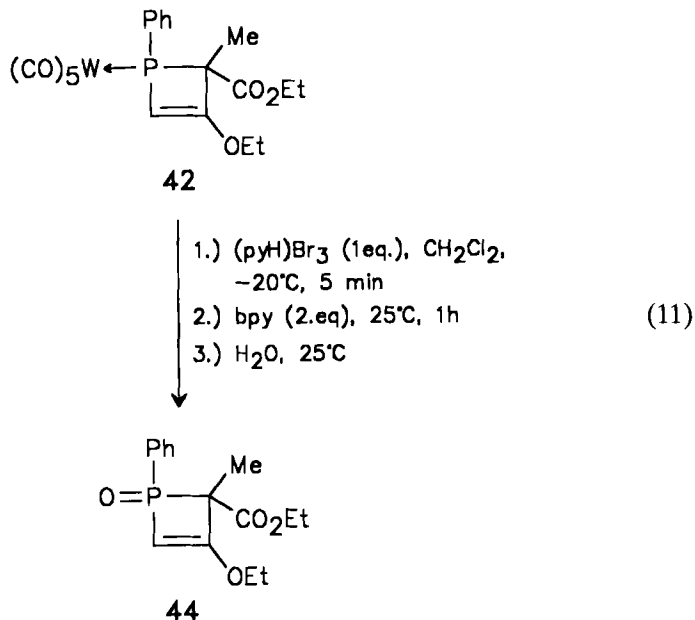
SCHEME 7.

to this, phosphalkene complexes **31-34** were prepared at low temperature via a phosphawittig reaction (Scheme 7). Compounds **35-38** are obtained as mixtures of two isomers. The $[\text{W}(\text{CO})_5]$ fragment imparts some stability to the electrophilic phosphalkenes, which in a free state do not exist under the reaction conditions. (See Table I.) Once again the removal of

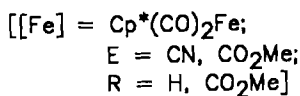
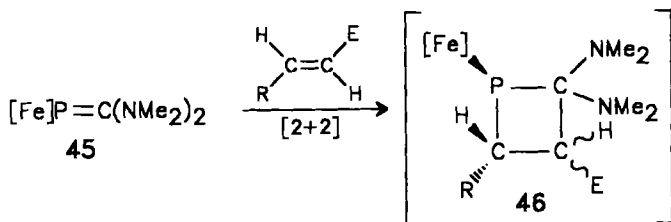
TABLE I
PHOSPHETANES AND 1,2-DIHYDROPHOSPHETES OBTAINED FROM PHOSPHAALKENE COMPLEXES

Compound	R ¹	R ²	R ³	Z	Yield (%)
31	Me	Me			
32	Ph	Me			
33	<i>t</i> -Bu	Me			
34	Ph	CO ₂ Et			
35	Me	Me	Et	NC ₅ H ₁₀	18
36	Ph	Me	Et	NC ₅ H ₁₀	80
37	<i>t</i> -Bu	Me	Et	NC ₅ H ₁₀	54
38	Ph	Me	H	OE _t	85
39	Me	Me	Me	NE _t ₂	68
40	Ph	Me	Me	NE _t ₂	64
41	Ph	CO ₂ Et	Me	NE _t ₂	70
42	Ph	Me	H	OE _t	74
43	Ph	CO ₂ Et	H	OE _t	37

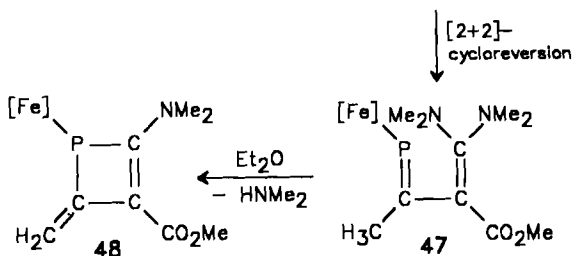
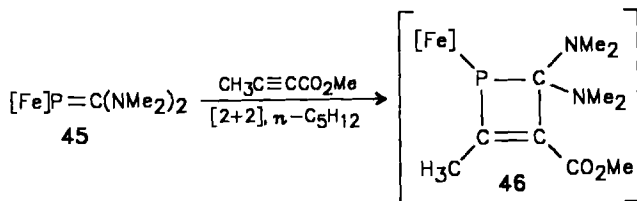
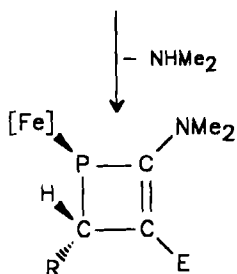
the carbonylmethyl moiety from the heterocycle is possible by reacting complex **42** with pyridinium tribromide, 2,2'-bipyridyl, and water to give the phosphetane *P*-oxide **44**; see Eq. (11).²¹



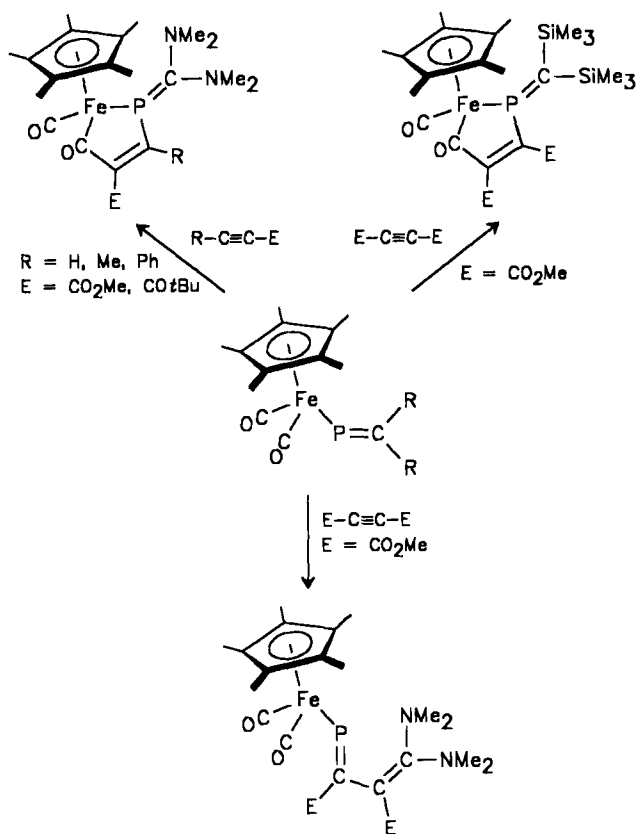
1,2-Dihydrophosphetes are also available by the action of the electron-rich metallophosphaalkene **45** with electron-deficient alkenes such as dimethyl fumarate, fumarodinitrile, and methyl acrylate, as shown in Eq. (12).²⁴ Ring formation is most likely initiated by a stepwise [2+2] cycloaddition and completed by rapid dimethylamine elimination from transient phosphetane **46**. The ferriophosphaalkene **45** is smoothly converted into 2-methylene 1,2-dihydrophosphete **48** by reaction with methyl butynoate in diethylether. If the reactants are mixed in *n*-pentane, a brown precipitate of 1-ferrio-1-phosphabutadiene **47** separates instead. This heterobutadiene spontaneously cyclizes to **48** with effervescence of dimethylamine when dissolved in THF, ether, or benzene (Scheme 8).²⁵



(12)



SCHEME 8.

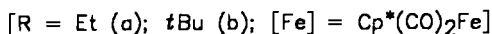
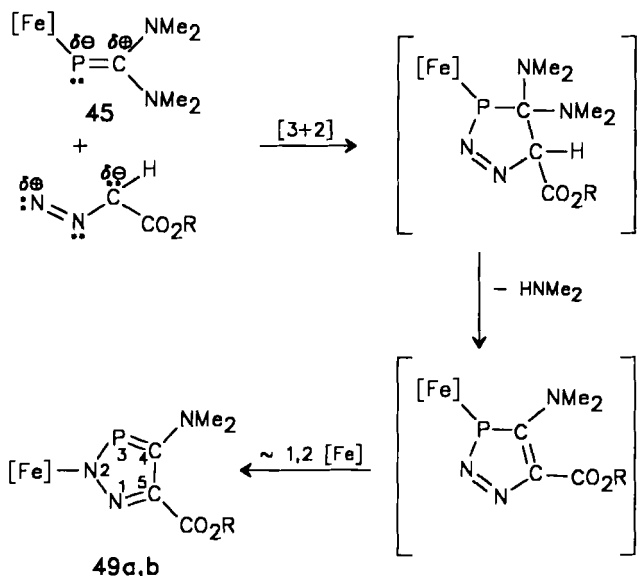


SCHEME 9.

A rationale for this reaction invokes an initial $[2+2]$ cycloaddition to **46**, which rapidly undergoes a $[2 + 2]$ cycloreversion to the poorly pentane-soluble 1-phosphabutadiene **47**.²⁵ The synthetic access to 1,2-dihydrophosphetes via metallocyclophosphalkenes and electron-poor alkynes is, however, of no general applicability. In a number of cases the combination of these reactants furnishes five-membered metallaheterocycles and/or stable 1-metallaphosphabutadienes, as depicted in Scheme 9.^{25,26}

C. Five-Membered Rings

Frequently, $[3+2]$ cycloadditions of 1,3-dipolar reagents such as PhN_3 , diazoalkanes, or nitrile oxides to acyclic phosphalkenes provides access



SCHEME 10.

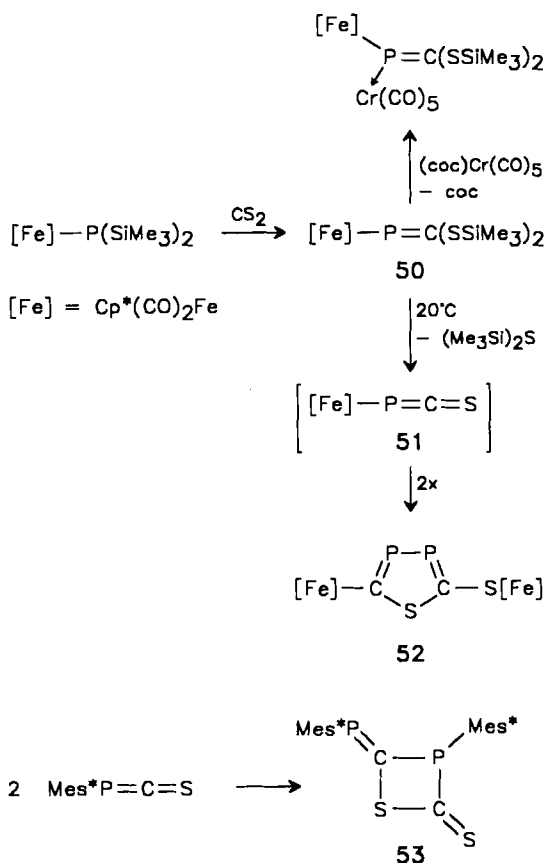
to five-membered phosphorus heterocycles.²⁷ In general, these processes take place without the assistance of transition-metal compounds. There are, however, a few phosphole derivatives, which are generated from acyclic $\text{P}=\text{C}$ systems present in the coordination sphere of transition-metal complexes.

Treatment of the metallophosphaalkene **45** with diazoacetates $\text{N}_2\text{CHCO}_2\text{R}$ ($\text{R} = \text{Et}, t\text{-Bu}$) affords the novel *N*-metalated 1,2,3-diazaphospholes **49a,b** as products of a dipolar $[3+2]$ cycloaddition, which is followed by amine elimination and a sigmatropic 1,2-shift of the metal-complex fragment from phosphorus to nitrogen (Scheme 10).²⁸ This result merits attention for several reasons:

- 1,3-Dipolar cycloadditions of acyldiazoalkanes with suitably 1,2-functionalized phosphalkenes such as $\text{Me}_3\text{Si}-\text{P}=\text{C}(\text{R})\text{OSiMe}_3$ or $\text{Cl}-\text{P}=\text{C}(\text{R})\text{SiMe}_3$ usually afford 1,2,4-diazaphospholes and not the 1,2,3-isomers described here.²⁹

2. The coordination chemistry of 1,2,3-diazaphospholes has been scarcely developed. It features a few P- and N-coordinated complexes where the ring invariantly donates two electrons by virtue of the respective lone pair.³⁰ Compounds **49a,b** are the first transition-metal derivatives of 2*H*-1,2,3-diazaphospholes where a 17-valence electron fragment is linked to the nitrogen atom N(2) in place of an organosubstituent.

The combination of equimolar amounts of $\text{Cp}^*(\text{CO})_2\text{FeP}(\text{SiMe}_3)_2$ and CS_2 leads to the metallophosphaalkene **50**, which is easily trapped by coordination to the $[\text{Cr}(\text{CO})_5]$ unit. Free **50** undergoes facile elimination of $(\text{Me}_3\text{Si})_2\text{S}$ with formation of 1,3,4-thiadiphosphole **52** (Scheme 11).³¹ Similar

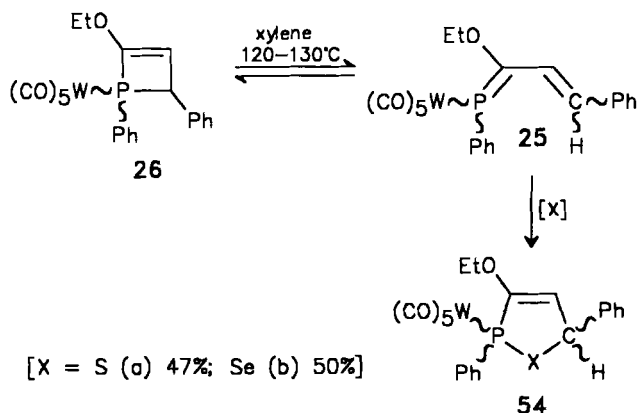


SCHEME 11.

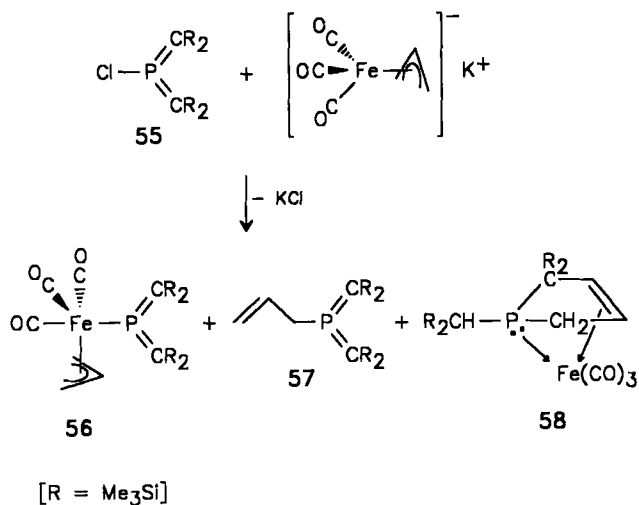
results are obtained by treating $\text{FeBr}(\text{CO})_2\text{Cp}^*$ with $[\text{Li}(\text{DME})_3][\text{SC}\equiv\text{P}]$.³¹ Compound **52** is the first 1,3,4-thiadiphosphole, although a few representatives of the isomeric 1,2,4-thiadiphosphole system have been described previously.^{32–36} The mechanism of this process remains unclear. It is conceivable, however, that the ring closure results from the dipolar [2+3] cycloaddition of two molecules of **51**. For comparison, it is interesting to note the dimerization of the hypothetical phosphathioketene $\text{Mes}^*\text{P}=\text{C}=\text{S}$ to a 1,3-thiaphosphetane **53** (Scheme 11).³⁷

Generally, 1,2-dihydrophosphetes and 1-phosphabutadienes coexist in an equilibrium, which may be shifted towards the acyclic species at elevated temperatures.³⁸ In accordance with this, the insertion of sulfur and selenium into the 1,2-dihydrophosphete ring of complex **26** at ca 120°C yields 2,5-dihydro-1,2-thiaphosphole **54a** and 2,5-dihydro-1,2-selenaphosphole **54b** a process most likely proceeding via complex **25** (Scheme 12).³⁹ Obviously, the $[\text{W}(\text{CO})_5]$ group imparts sufficient stability to **25**, thus facilitating the ring-opening process.

Reaction of chlorobis(methylene)phosphorane **55** with $\text{K}[(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3]$ in a mixture of THF and toluene gives the metallobis(methylene)phosphorane **56** and the bis(methylene)propenylphosphorane **57** as major products. The dihydrophosphole complex **58** is obtained as a minor product (<10% yield) (Scheme 13).⁴⁰ In contrast, treatment of **55** with $\text{K}[\text{Fe}(\text{CO})_2\text{Cp}]$ gives rise to the formation of the metallobis(methylene)phosphorane **59** (39% yield) and the phosphaferrrocene **60** (34–72% yield, dependent upon the reaction time). The phosphole ligand of **60** is con-

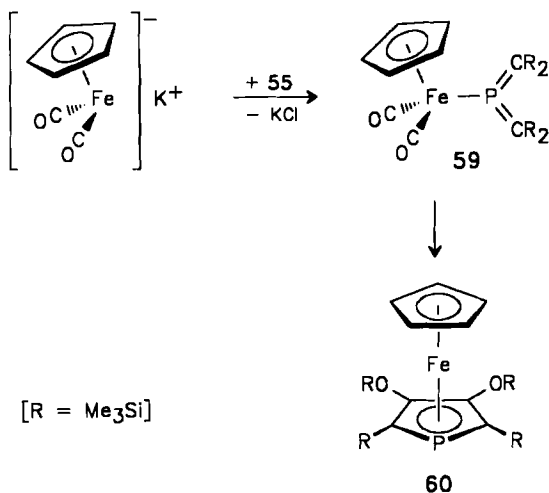


SCHEME 12.

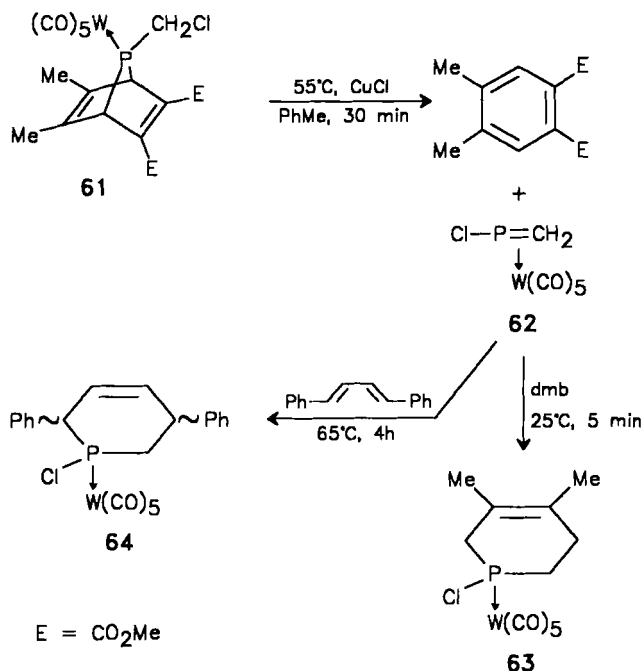


SCHEME 13.

structed by cocyclization of all acyclic ligands present in **59**, with the CpFe unit serving as a template (Scheme 14).⁴⁰ The synthesis of the related 1,2-diphosphaferrocenes from 1-metallo-1,2-diphosphapropenes has been discussed earlier and shown in Eqs. (5)–(7).



SCHEME 14.



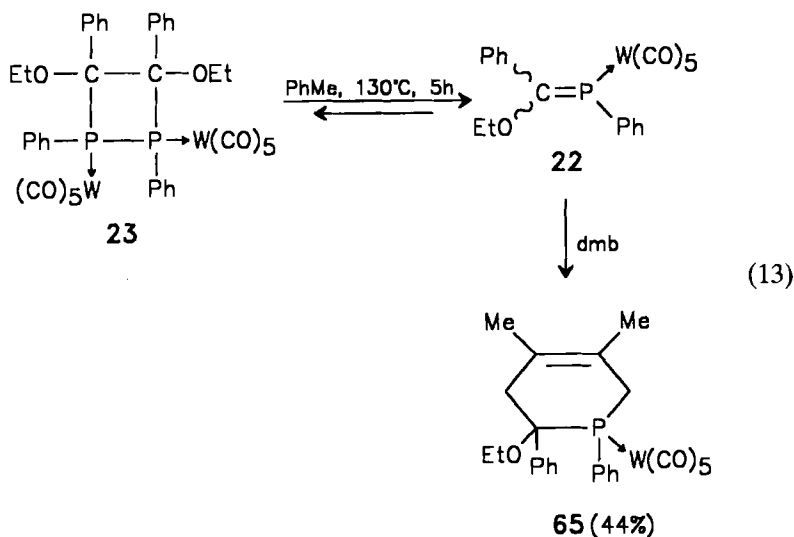
SCHEME 15.

D. Six-Membered Rings

The [2+4] cycloaddition of 1,3-dienes to reactive phosphaaalkenes is a well-established method for the chemical proof of such transient species. Moreover, this type of reaction provides an elegant and convenient entry into the class of six-membered phosphorus heterocycles.⁴¹ In many cases the presence of a transient-metal-complex fragment seems to be of advantage to stabilize either the phosphaaalkene or its reactive precursor. This is impressively illustrated in the copper(I)-chloride-catalyzed thermolysis of the 7-phosphanorbornadiene-tungsten carbonyl complex **61** to give the η^2 -phosphaaalkene complex **62**.⁴² Free methylenechlorophosphane is unstable and has only been transiently characterized in the dehydrochlorination of methyldichlorophosphane either by heat^{43a} or by nitrogen bases.^{43b} Obviously, π -coordination of the $\text{P}=\text{C}$ double bond drastically stabilizes this molecule. Thus, complex **62** can be heated to 65°C without decomposition. The $\text{P}=\text{C}$

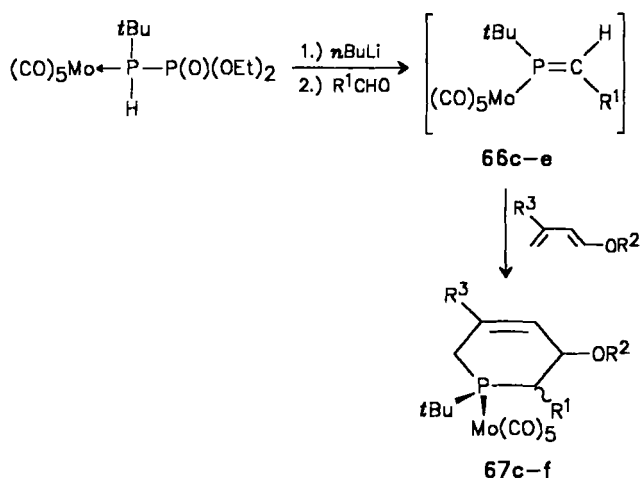
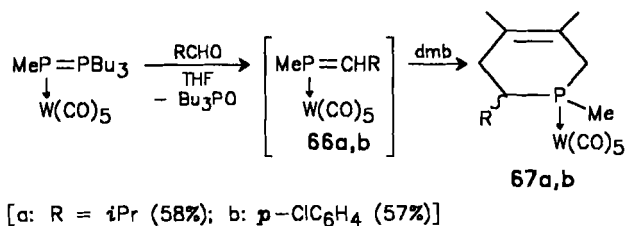
bond in **62** is sufficiently reactive to be involved in Diels–Alder cycloadditions with 2,3-dimethylbutadiene at 25°C or with 1,4-diphenylbutadiene at 65°C to yield tetrahydroposphinanes **63** and **64**, respectively. These observations are readily explained by an equilibrium between the η^1 - and η^2 -coordination of the phosphalkene. In an η^1 -complex the unsupported P=C double bond is available for addition reactions (Scheme 15).⁴²

As previously mentioned, at elevated temperatures the 1,2-diphosphatane **23** is in equilibrium with η^1 -phosphalkene tungsten complex **22** (Scheme 5). Interception of **22** with 2,3-dimethylbutadiene to heterocycle **65** is achieved in benzene at 130°C; see Eq. (13).¹⁷



Reactive η^1 -phosphalkene tungsten complexes such as **66**, which are accessible by the phosphawittig route, are appropriate candidates for cycloadditions, as illustrated in Scheme 16.^{20,22}

Attempts to trap *P*-*tert*-butyl substituted phosphalkene complexes **66c–e** with 2,3-dimethylbutadiene have been unsuccessful, owing to the poor reactivity of the diene at low temperatures. This limitation is circumvented when the respective *t*-butyl-substituted complexes are exposed to electron-rich acyclic dienes such as 1-methoxy-1,3-butadiene, 1-(trimethylsilyloxy)-1,3-butadiene, and 1-methoxy-3-(trimethylsilyloxy)-



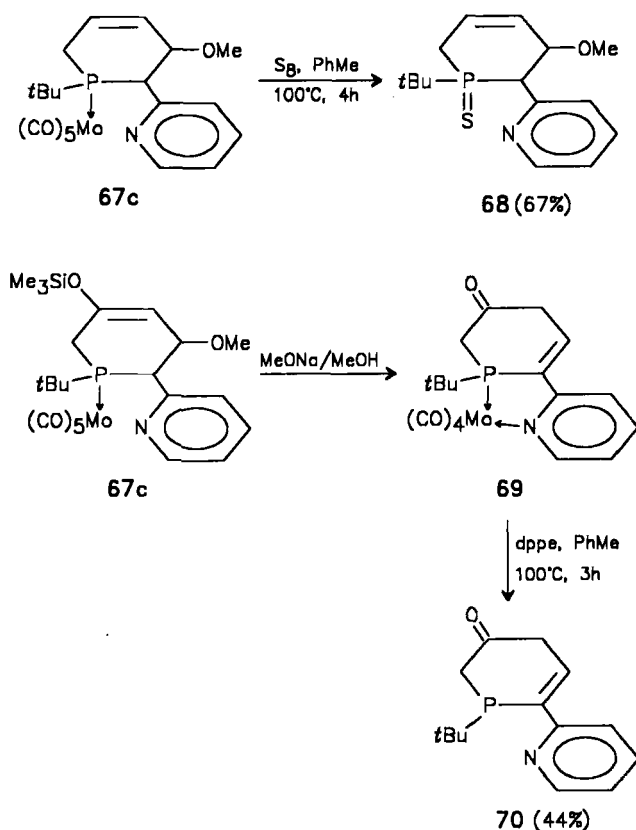
SCHEME 16.

1,3-butadiene to afford tetrahydrophosphinine complexes **67c–f** in the temperature range from -78 to 25°C (Scheme 16, Table II).^{44a} The products are obtained as single isomers, which reflects the excellent stereocontrol of this process.

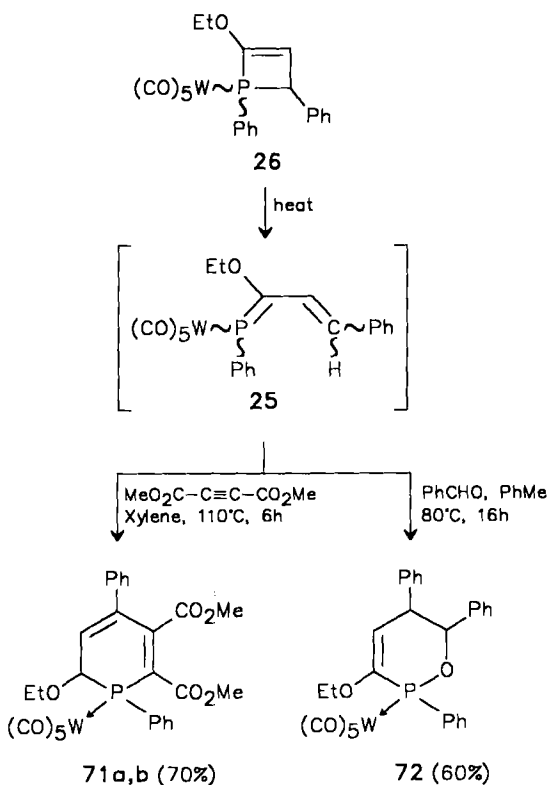
TABLE II
TETRAHYDROPHOSPHININE COMPLEXES OBTAINED FROM
PHOSPHAALKENE COMPLEXES AND 1,3-DIENES

Product	Precursor	R ¹	R ²	R ³	Yield (%)
67c	66c	2-py	OMe	H	63
67d	66c	2-py	OMe	OSiMe ₃	69
67e	66d	6-methyl-2-pyridyl	OSiMe ₃	H	40
67f	66e	2-thienyl	OMe	OSiMe ₃	50

The various heterocyclic ligands just described are easily cleaved from the respective molybdenum centers either by reaction with sulfur or through ligand exchange with 1,2-bis(diphenylphosphino)ethane (Scheme 17).^{44a} The Diels–Alder cycloaddition is successfully expanded to transient 1-phospha-1,3-diene complexes such as **25** and suitable dienophiles. As illustrated in Scheme 12, the isomeric 1,2-dihydrophosphetes (e.g., **26**) are their masked stable precursors. Reaction of **26** with dimethyl acetylenedicarboxylate or with benzaldehyde furnishes the Diels–Alder adducts of transient **25**, compound **71**, as a mixture of two isomers, and isomerically pure **72**.^{44b} (See Scheme 18.)



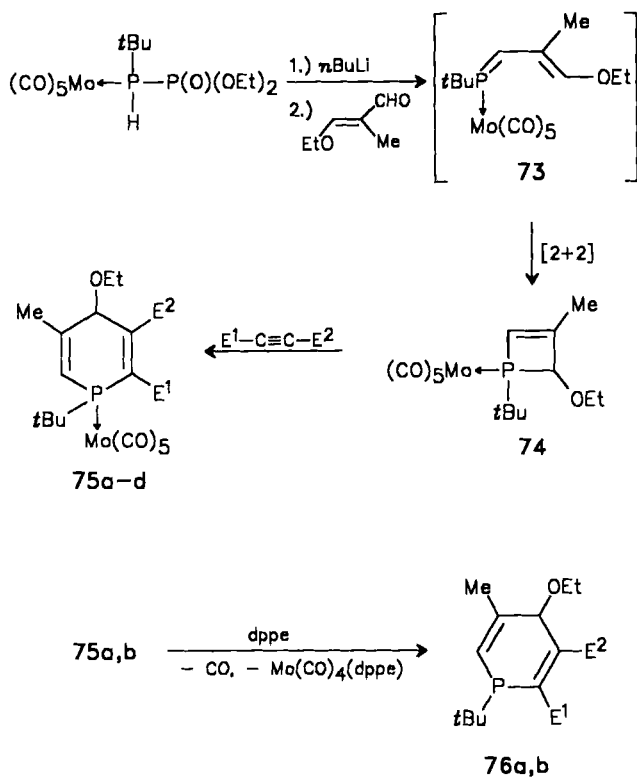
SCHEME 17.



SCHEME 18.

Compound **74**, which results from a phospho-Wittig reaction via the 1-phospha-1,3-butadiene complex **73**, according to Scheme 19, is even more reactive toward alkynes than **26** or **25**, respectively. The complex smoothly reacts with alkynes to afford the 1,4-dihydrophosphinine complexes **75a-d**. In the case of unsymmetrical alkynes, the cycloaddition is regioselective and seems to be controlled by steric rather than by electronic factors. Less electron-rich 1,2-dihydrophosphete complexes with alkyl or phenyl substituents in the 3- and 4-positions are not sufficiently reactive toward alkynes.⁴⁴

Liberation of the 1,4-dihydrophosphinines **76a,b** thus synthesized is accomplished by heating carbonyl molybdenum complexes **75a,b** in the pres-



SCHEME 19.

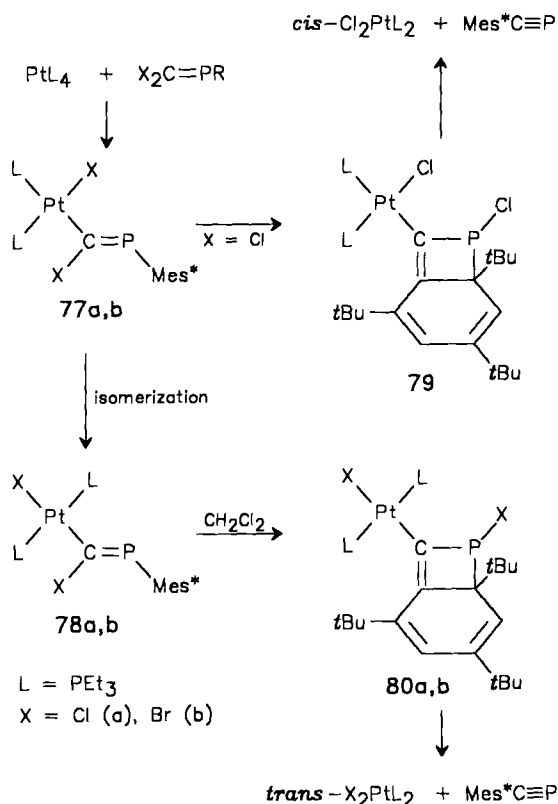
ence of 1,2-bis(diphenylphosphino)ethane (Scheme 19, Table III).⁴⁴ These cycloadditions provide an effective access to novel highly functionalized phosphinines.⁴⁴

TABLE III
1,4-DIHYDROPHOSPHININE COMPLEXES OBTAINED FROM
A TRANSIENT 1-PHOSPHA-1,3-DIENE COMPLEX AND ALKYNES

Compound	E ¹	E ²	Conditions	Yield (%)
75a	CO ₂ Me	CO ₂ Me	40°C, 4 h	60
75b	CO ₂ Et	Ph	80°C, 24 h	45
75c	H	Ph	75°C, 2 h	36
75d	H	2-py	70°C, 1 h	30

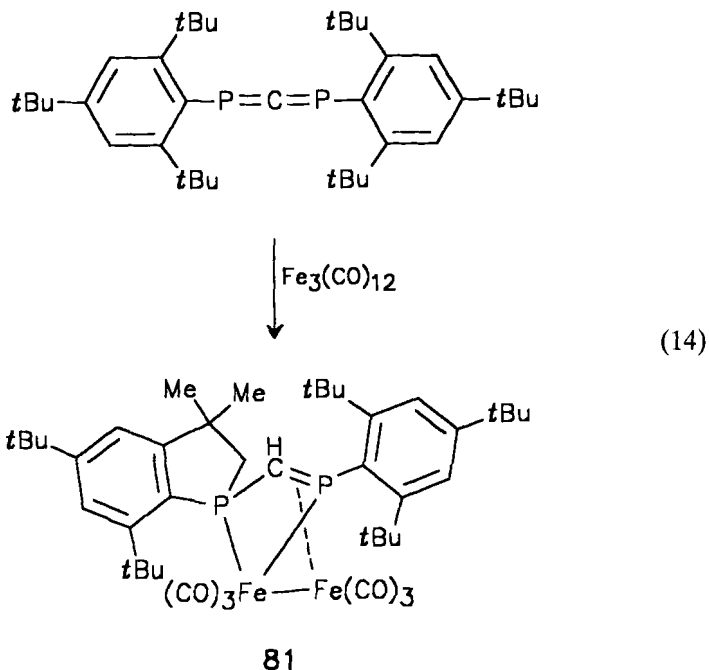
E. Polycyclic Compounds

Oxidative addition reactions of $\text{Pt}(\text{PEt}_3)_4$ with the dihalomethylene phosphanes $\text{X}_2\text{C}=\text{PMes}^*$ ($\text{X} = \text{Cl}, \text{Br}$) initially yield the *cis*-isomer of the platinomethylene phosphanes **77a,b**. The chloro derivative **77a** can be isolated from a hexane solution at -50°C . In the presence of free PEt_3 , compounds **77a,b** rapidly rearrange to give the *trans*-isomers **78a,b**. In polar solvents (CH_2Cl_2 and CHCl_3), complexes **77** and **78a,b** are converted to phosphaaalkyne $\text{Mes}^*\text{C}\equiv\text{P}$ and *cis*- and *trans*- $\text{X}_2\text{Pt}(\text{PEt}_3)_2$, respectively, via the bicyclic intermediates **79** and **80**. In contrast with the labile *cis*-isomer **79**, the *trans*-compounds **80a,b** can be isolated and fully characterized. According to an X-ray diffraction study, **80a** features a 1,2-dihydrophosphete which is fused to a 1,3-cyclohexadiene ring via the carbon atoms C2 and C3 (Scheme 20).⁴⁵



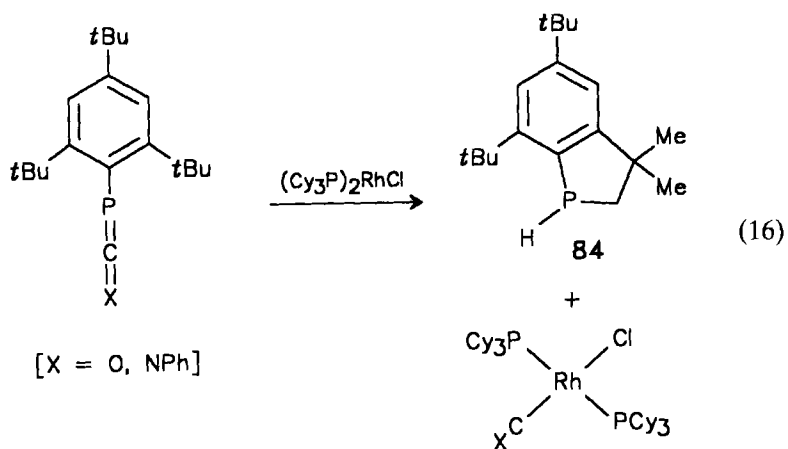
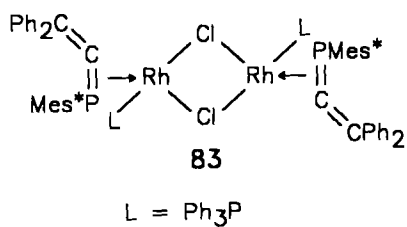
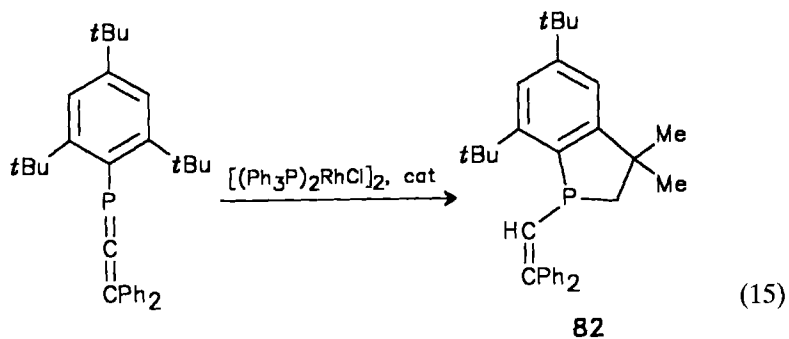
SCHEME 20.

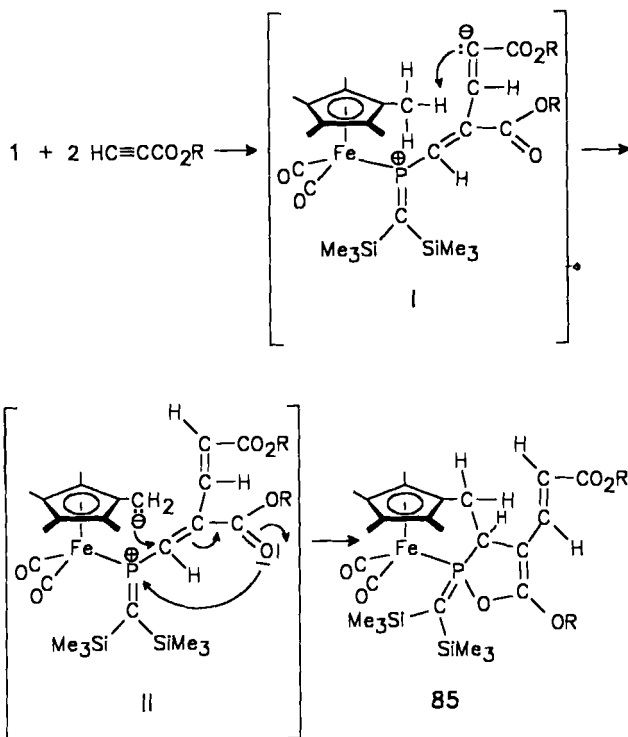
The carbonyliron-assisted rearrangement of diphosphaallene $\text{Mes}^* \text{P}=\text{C}=\text{PMes}^*$ formally involves the oxidative addition of a CH-bond of a *t*-butyl group across the $\text{P}=\text{C}$ double bond to afford the dinuclear complex **81**. One phosphorus atom of the 1,3-diphosphapropene-like ligand of **81** participates in a dihydrophosphaindane skeleton; see Eq. (14).⁴⁶



The quantitative conversion of the phosphaaallene $\text{Mes}^* \text{P}=\text{C}=\text{CPh}_2$ into phosphaindane **82** occurs upon heating the compound in THF at 50°C for 7 days in the presence of catalytic amounts of $[(\text{Ph}_3\text{P})_2\text{RhCl}]_2$; see Eq. (15).⁴⁷ According to ^{31}P NMR studies, complex **83** ($\text{L} = \text{PPh}_3$) is the catalytically active species. The more stable analog of **83** with $\text{L} = \text{P}(c\text{-Cy})_3$ is isolable from the reaction mixture.⁴⁷

Treatment of $[(c\text{-C}_6\text{H}_{11})_3\text{P}]_2\text{RhCl}$ with the phosphacumulenes $\text{Mes}^* \text{P}=\text{C}=\text{X}$ ($\text{X} = \text{O}, \text{NPh}$) results in $\text{P}=\text{C}$ bond cleavage to form the phosphaindane **84** and *trans* $[(c\text{-C}_6\text{H}_{11})_3\text{P}]_2\text{RhCl}(\text{CX})$ ($\text{X} = \text{O}, \text{NPh}$); see Eq. (16).⁴⁷

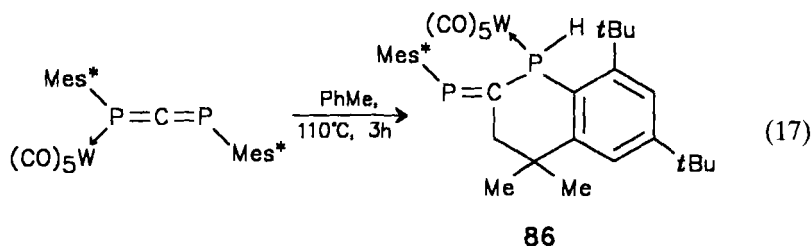




SCHEME 21.

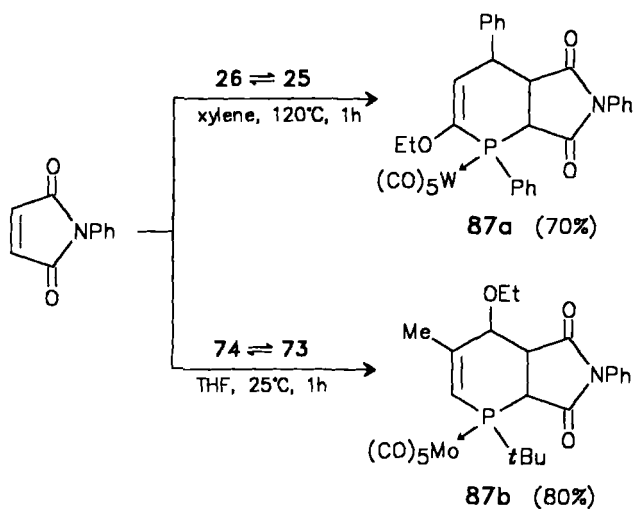
A fused ligand system with a 1,2-dihydro-2-oxaphosphole unit is obtained by treating the metallophosphaalkene $\text{Cp}^*(\text{CO})_2\text{FeP}=\text{C}(\text{SiMe}_3)_2$ (**1**) with two molar equivalents of alkyl propiolates in *n*-pentane (Scheme 21).⁴⁸ Although no intermediates are detectable, it is conceivable that the generation of the bicyclic ylide **85** is initiated by nucleophilic addition of the phosphorus atom of **1** to two molecules of alkyne. Transprotonation in transient **I** gives the zwitterion **II**, which collapses to product **85** via carbanion attack at the carbon atom α to the phophenium center, with subsequent P—O bond formation.⁴⁸

In boiling toluene, the 1,3-diphosphaallene complex $\text{Mes}^*\text{P}[\text{W}(\text{CO})_5]=\text{C}=\text{PMes}^*$ undergoes a hydrogen migration from carbon to phosphorus to afford the tetrahydro-1-phosphanaphthalene complex **86**; see Eq. (17).⁴⁶



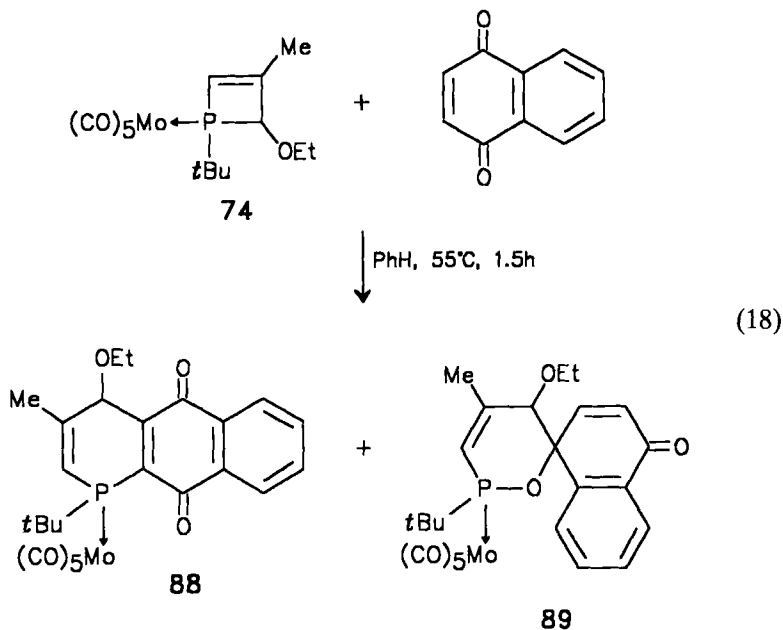
The Diels-Alder addition of the 1,2-dihydrophosphete complexes **26** and **74** to *N*-phenylmaleimide proceeds smoothly, yielding the bicyclic species **87a** and **87b**. The improved reactivity of **74** over **26** is reflected by the considerably milder reaction conditions (Scheme 22).^{44a,b}

Electron-poorer 1,2-dihydrophosphete complexes with alkyl and phenyl substituents at the ring skeleton are inert towards *N*-phenylmaleimide.^{44a} The reaction of **74** with 1,4-naphthoquinone in benzene at 55°C leads to

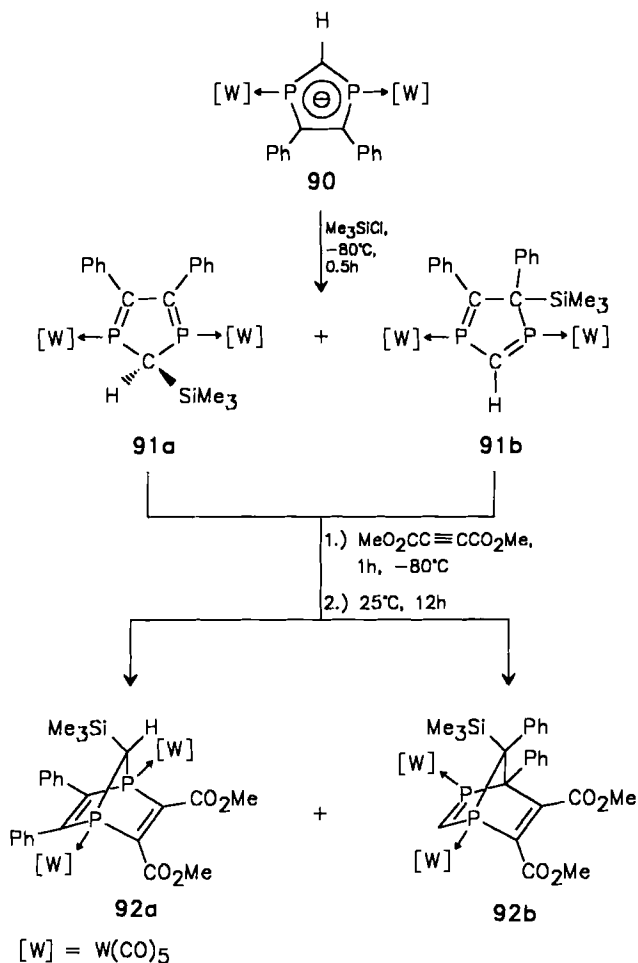


SCHEME 22.

a mixture of three products as a result of cycloadditions at either the carbon-carbon double bond (**88**) or the carbonyl function (**89a,b**); see Eq. (18).

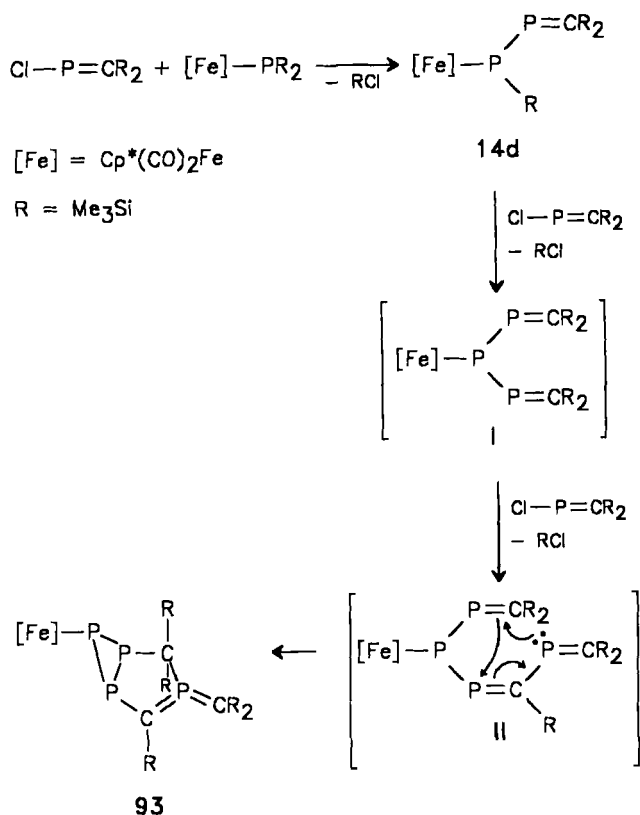


A spirocyclic derivative analogous to **89** is formed as a 7:3 mixture of two isomers from benzoquinone and $(\text{CO})_5\text{MoP}(\text{t-Bu})\text{CH}=\text{C}(\text{Me})\text{CHPh}$ in xylene at 110°C.^{44a} Bicyclic compounds such as **92a** and **92b** with two phosphorus atoms are accessible from the bis(pentacarbonyltungsten) complex of a 1,3-diphospholide anion **90**. At -80°C, the anion **90** is silylated by chlorotrimethylsilane, and the resulting mixture of phospholes **91a** and **91b** produced is treated with dimethyl acetylenedicarboxylate to yield [4+2] cycloadducts **92a** and **92b** in a 40:60 ratio (Scheme 23). As the ratio of products does not change with reaction time at -80°C, it is assumed that a 40:60 mixture of phospholes is also generated before alkyne interception. At 25°C, the same reaction yields only the cycloadduct **92a**. Usually, 1,5-sigmatropy in cyclopentadienyls and related systems is a facile process even at low temperature. Thus, here, the role of the transition-metal-complex fragments is to inhibit these sigmatropic shifts.⁴⁹



SCHEME 23.

Reaction of $\text{Cp}^*(\text{CO})_2\text{FeP}(\text{SiMe}_3)_2$ with 3 $\text{ClP}=\text{C}(\text{SiMe}_3)_2$ in THF at 20°C leads to the formation of the red crystalline 3-methanediyl-1,3,5,6-tetraphosphabicyclo[3.1.0]hex-2-ene compound **93**. It is assumed that the initially formed ferriodiphosphapropene **14d** is converted to 2,3,4-triphosphapentadiene **I** by means of a second molecule of the chlorophosphaalkene. Condensation of **I** with the third equivalent of phosphoalkene generates transient 2,4,5,6-tetraphosphahepta-1,3,6-triene **II**, which cyclizes to product **93** (Scheme 24).⁵⁰

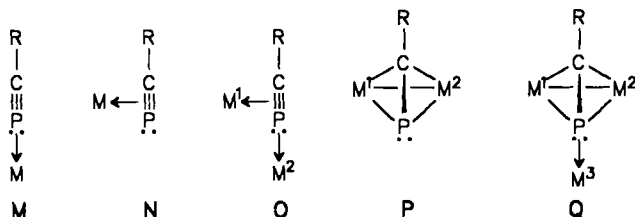


SCHEME 24.

IV

PHOSPHAALKYNES AS LIGANDS IN TRANSITION-METAL COMPLEXES

Phosphaalkynes $\text{RC}\equiv\text{P}$ display a rich coordination chemistry, and five different modes of ligation (**M-Q**) may be discerned in phosphaalkyne transition-metal complexes (Scheme 25).^{3,51} According to theoretical calculations and to photoelectron spectroscopic investigations, the doubly degenerated π -orbitals of the triple bond are the HOMOs in phosphaalkynes. In keeping with this, the η^2 -coordination modes **N-Q** are usually realized with transition metals. Complexes with η^1 -ligated phosphaalkynes **M** are only possible when the respective ensemble of metal atom and ancillary ligands form an appropriate pocket, which only allows η^1 -coordination by a linear molecule.^{3,51}



SCHEME 25.

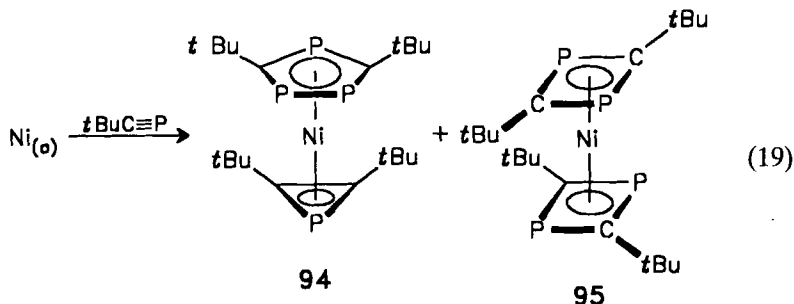
V

RINGS AND CAGES FROM PHOSPHAALKYNES

The following section describes metal-assisted syntheses of rings and cages from phosphalkynes. The phosphalkyne may either become part of a well-defined transition-metal complex, or alternatively react with metal centers in a cocondensation process. Moreover, it is possible for phosphalkynes to oligomerize or cooligomerize with other molecules in the coordination sphere of a metal complex. Detachment of the newly constructed ligands is not in all cases possible.

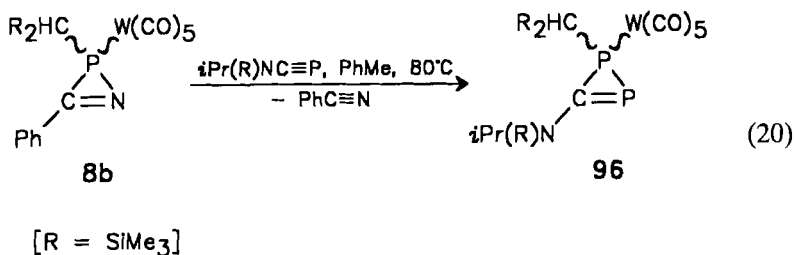
A. Three-Membered Rings

Cocondensation of nickel atoms, generated by metal vapor synthesis techniques with $t\text{-BuC}\equiv\text{P}$, affords equal amounts of the isomeric sandwich complexes **94** and **95**. The former compound features an η^3 -phosphirenyl ligand in addition to an η^5 -1,2,4-triphospholyl ring, whereas in **95** the metal is sandwiched between two η^4 -1,3-diphosphete units; see Eq. (19).^{51c}



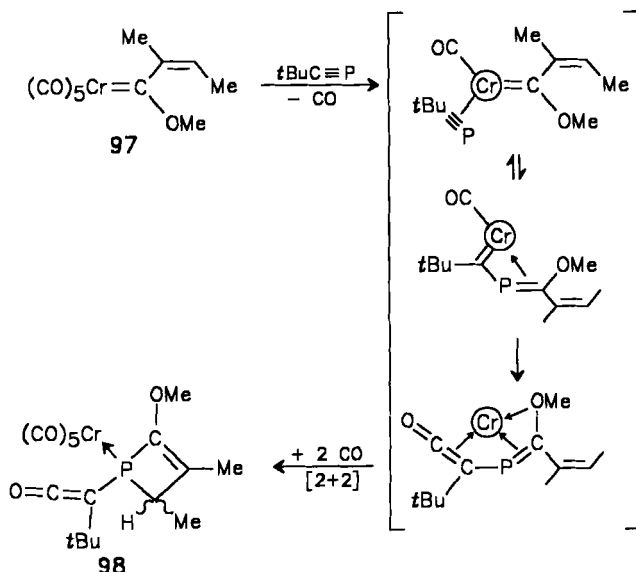
The nature of the complexes, synthesized from metal vapor and $t\text{-BuC}\equiv\text{P}$, is highly dependent upon the nature of the metal. Thus, with iron, chromium, or vanadium atoms, pentaphosphametalloenes are obtained.⁵¹ In contrast, the phosphalkyne and molybdenum or tungsten atoms afford homoleptic tris[η^4 -1,3-diphosphete] metal(0) complexes $[\text{M}(\eta^4\text{-P}_2\text{C}_2\text{-}t\text{-Bu}_2)_3]$ ($\text{M} = \text{Mo}, \text{W}$).⁵¹

Reaction of the azaphosphirene complex **8b** with $i\text{-Pr}(\text{Me}_3\text{Si})\text{NC}\equiv\text{P}$ leads to the displacement of benzonitrile with incorporation of the phosphalkyne to give **96** as a representative of the rare class of diphosphirene complexes, as shown in Eq. (20).⁵²



B. Four-Membered Rings

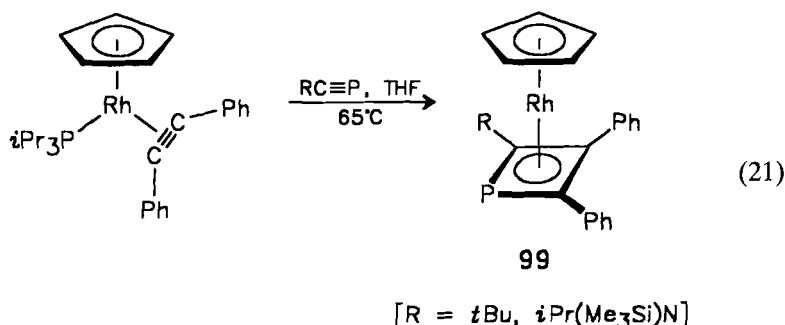
Peripheral reactions of organometallic complexes with phosphalkynes give access to a variety of four-membered organophosphor ring ligands.



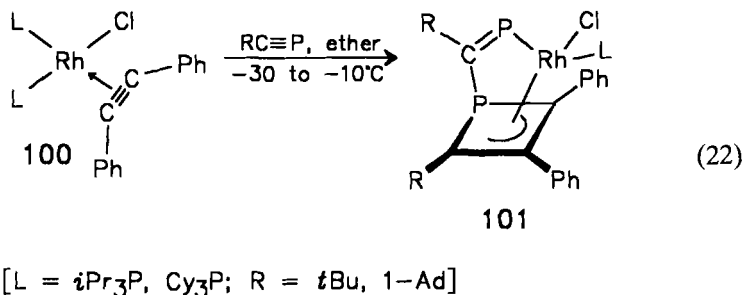
SCHEME 26.

Treatment of the vinylcarbene chromium complex **97** with $t\text{-BuC}\equiv\text{P}$ affords the dihydrophosphetylketene complex **98** (Scheme 26). This transformation is believed to proceed via η^2 -phosphaalkyne carbene-, phosphaalkenylcarbene-, and phosphaalkenylketene complexes as intermediates. An intramolecular [2+2] cycloaddition completes the reaction sequence.⁵³ Different carbene/carbon monoxide/phosphaalkyne cycloaddition products (e.g., 1,3-oxaphospholes, phosphaphenanthrenes) are obtained depending on substitution at the carbene ligand (vide infra).

Codimerizations of phosphaalkynes with a η^2 -ligated alkyne in rhodium complexes leads to η^4 -phosphete complexes such as **99**; see Eq. (21).⁵⁴



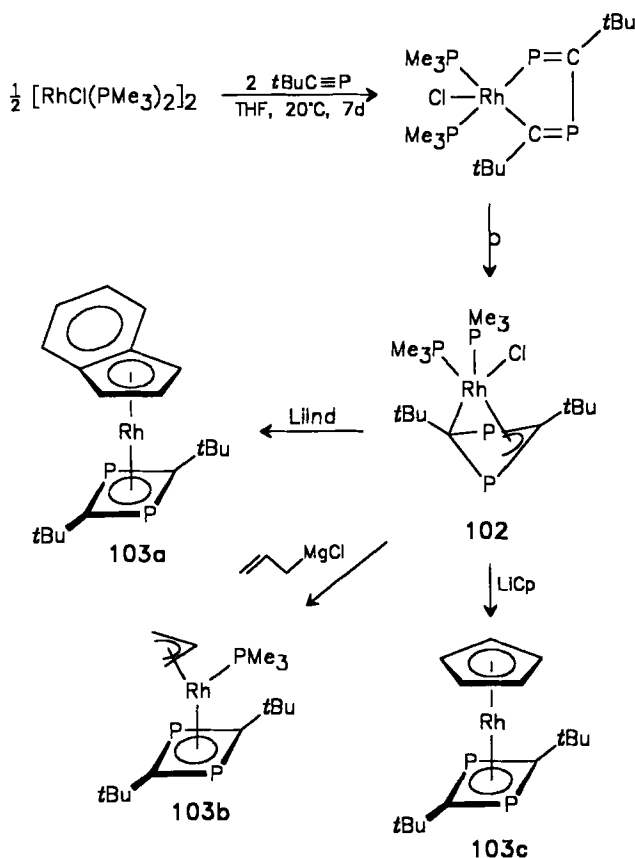
This type of process is sensitive to the nature of the ancillary ligands of the rhodium complex precursor, as well as to the substitution pattern of the alkyne ligand. Thus, the bis-phosphanerhodium complexes **100** ($L = i\text{-Pr}_3\text{P}$, Cy_3P) in ether combine with two equivalents of phosphaalkyne ($R = t\text{-Bu}$, 1-Ad) to yield the η^3 -phosphacyclobutenyl complex **101** containing an exocyclic phosphaalkenyl arm as shown in Eq. (22).^{54,55} The η^2 -dimethyl acetylenedicarboxylate ligand has also been employed in this transformation.



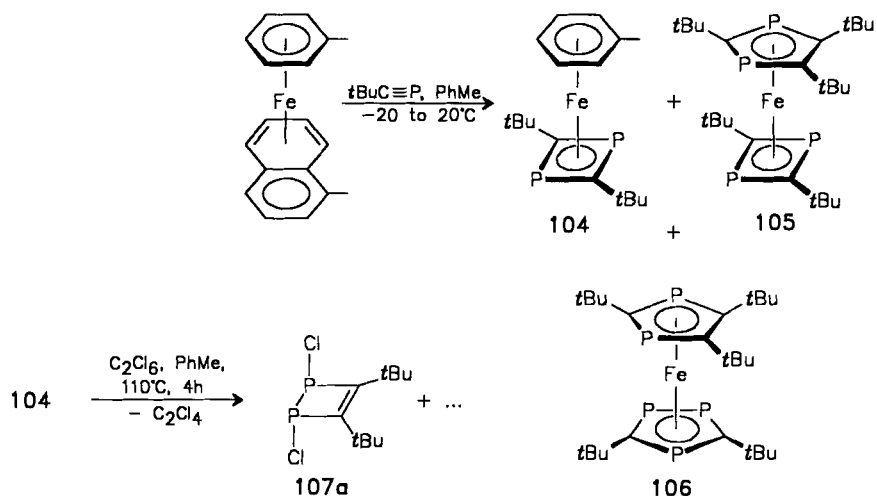
The reaction fails with η^2 -alkyne complexes containing H, Me_3Si , or alkyl substituents, owing to their instability or to their tendency to rearrange to

vinylidene complexes.⁵⁵ Less bulky phosphine ligands (e.g., PMe_3) in the precursor create a situation where incorporation of two molecules of the phosphalkyne furnishes a rhodadiphosphacyclopentadiene, which slowly rearranges to the $\eta^1 : \eta^3$ -1,3-diphosphacyclobutenyl complex **102**. The latter is smoothly converted into molecules **103a–c** with η^4 -1,3-diphosphete ligands, when subjected to reaction with allyl magnesium chloride, or indenyl- or cyclopentadienyllithium (Scheme 27).⁵⁶ The cyclodimerization to η^4 -1,3-diphosphete ligands is the most frequently observed reaction of phosphalkynes in the coordination sphere of transition metals.⁵⁰

Treatment of a toluene solution of $(\eta^6\text{-toluene})(\eta^4\text{-1-methylnaphthalene})\text{iron}(0)$ with 3.5 eq of $t\text{-BuC}\equiv\text{P}$ in the range from -20°C to ambient temperature affords a mixture of the sandwich complexes **104**, **105**, and **106**, from which orange crystals of **104** are separated in 48% yield (Scheme

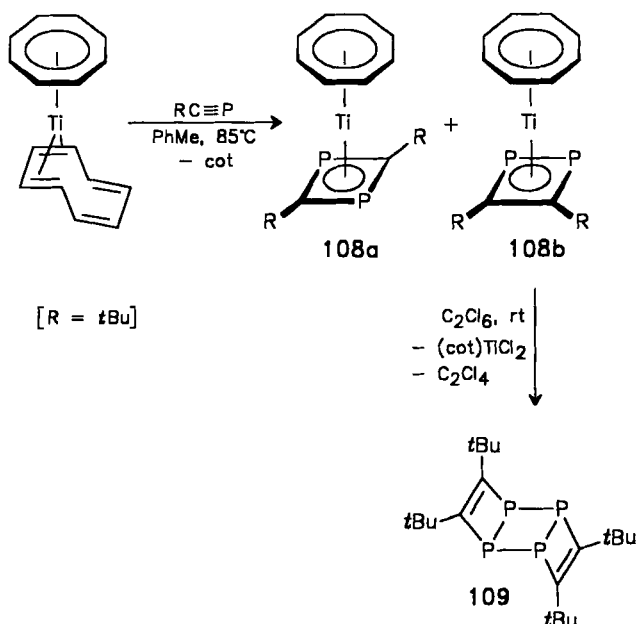


SCHEME 27.



SCHEME 28.

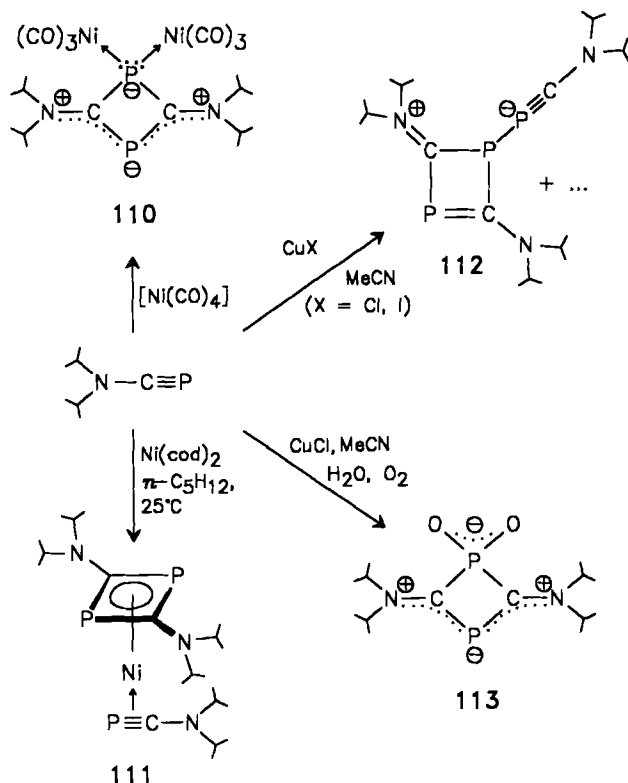
28).^{57a,b} Attempts to release the organophosphorus ligand by oxidation with hexachloroethane in boiling toluene furnished a 49% yield of the dichlorinated 1,2-dihydro-1,2-diphosphete complex **107** (Scheme 28).^{57c} In-



SCHEME 29.

terestingly, the exposure of bis(cyclooctatetraene)titanium to two molar equivalents of $t\text{-BuC}\equiv\text{P}$ or $1\text{-AdC}\equiv\text{P}$ affords an isomeric mixture of complexes **102** and **103** containing $\eta^4\text{-1,3-}$ as well as $\eta^4\text{-1,2-}$ diphosphete ligands in a ratio of about 55:45 (Scheme 29). In the case of the *tert*-butyl derivatives, separation of the isomers is achieved by oxidation with C_2Cl_6 ; only isomer **108b** is attacked and converted into $(\text{cot})\text{TiCl}_2$ and tricyclic **109** (Scheme 29).^{55,58} With $i\text{-Pr}(\text{Me}_3\text{Si})\text{N}-\text{C}\equiv\text{P}$, the corresponding reaction yields cleanly the 1,3-diphosphete complex analogous to **108a** [$\text{R} = i\text{-Pr}(\text{Me}_3\text{Si})\text{N}$].⁵⁸

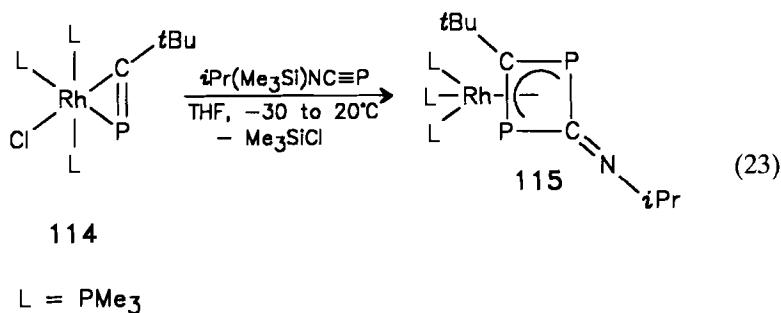
When the phosphalkyne $i\text{-Pr}_2\text{N}-\text{C}\equiv\text{P}$ is allowed to react with nickel-tetracarbonyl, the dinuclear zwitterionic complex **110** is formed (Scheme 30).^{59a} The reaction of a fourfold excess of the phosphalkyne with $\text{Ni}(\text{cod})_2$ or $\text{Ni}(\text{CO})_3(1\text{-aza}[2.2.2]\text{bicyclooctane})$ proceeds differently and produces the $(\eta^2\text{-phosphalkyne})(\eta^4\text{-1,3-diphosphete})$ complex **111**. Noncoordinated rings are isolated from the action of equimolar amounts of $i\text{-Pr}_2\text{N}-\text{C}\equiv\text{P}$



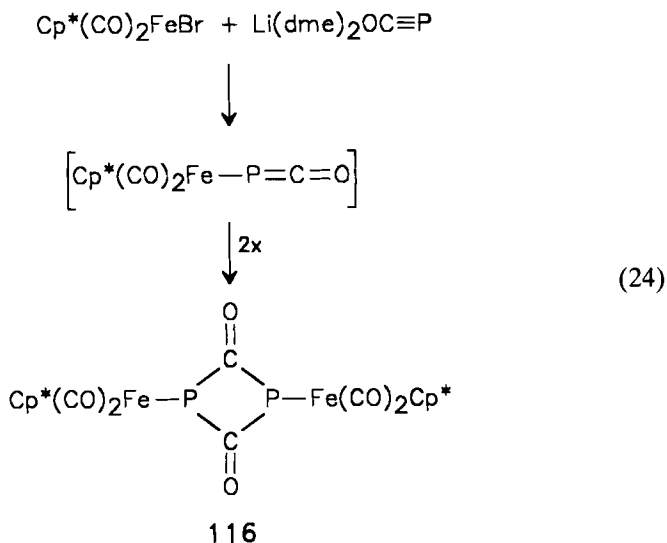
SCHEME 30.

and CuCl or CuI in acetonitrile. Under anaerobic conditions the reaction gives a complex mixture of phosphorus-containing species, one of which is identified as the unusual trimer **112**.^{59b,c} However, if the reaction is conducted in the presence of air and moisture, the four-membered ring species **113** is obtained as the sole isolable product (20% yield). The role of the copper compound is clearly that of a catalyst.^{59b}

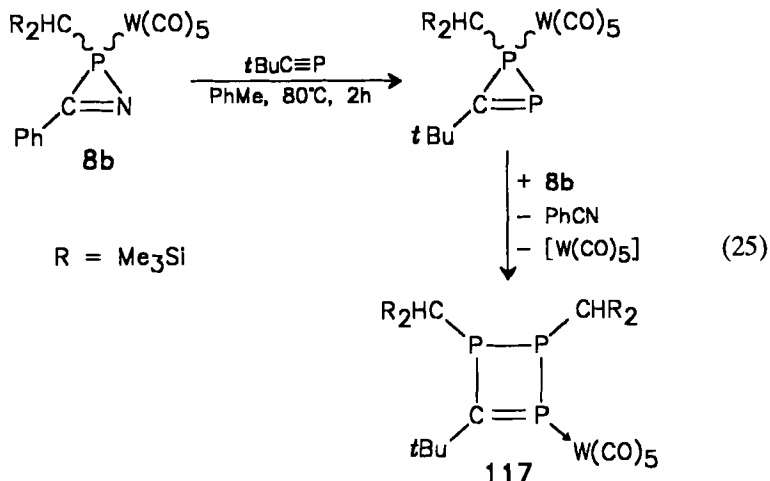
The codimerization of two different phosphalkynes is realized in the reaction between the η^2 -phosphalkyne complex **114** and $i\text{-Pr}(\text{Me}_3\text{Si})\text{N}-\text{C}\equiv\text{P}$. The preparation of **115** is accompanied by Me_3SiCl elimination and the formation of an exocyclic imino function; see Eq. (23).^{56c}



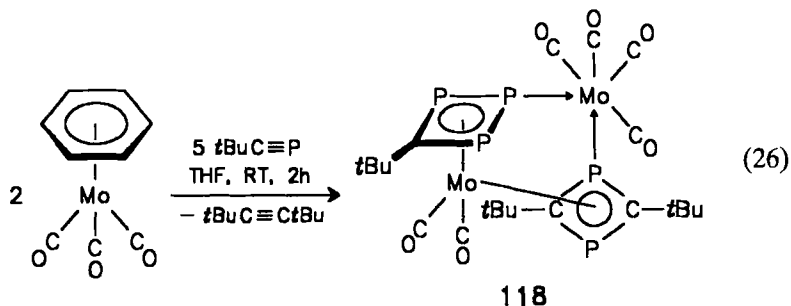
A dimerization of a transient metallophosphaketene to form **116** is observed when the lithioxyphosphalkyne $\text{Li}(\text{dme})_2\text{OC}\equiv\text{P}$ interacts with $\text{FeBr}(\text{CO})_2\text{Cp}^*$, as shown in Eq. (24).⁶⁰



The 1,2-dihydro-1,2,3-triphosphetate complex **117** is isolated from the reaction of **8b** with $t\text{-BuC}\equiv\text{P}$ in toluene at 80°C . In contrast with the formation of **96**, a second phosphinidene unit is incorporated into the respective 1-*H*-diphosphirene complex; see Eq. (25).⁵²



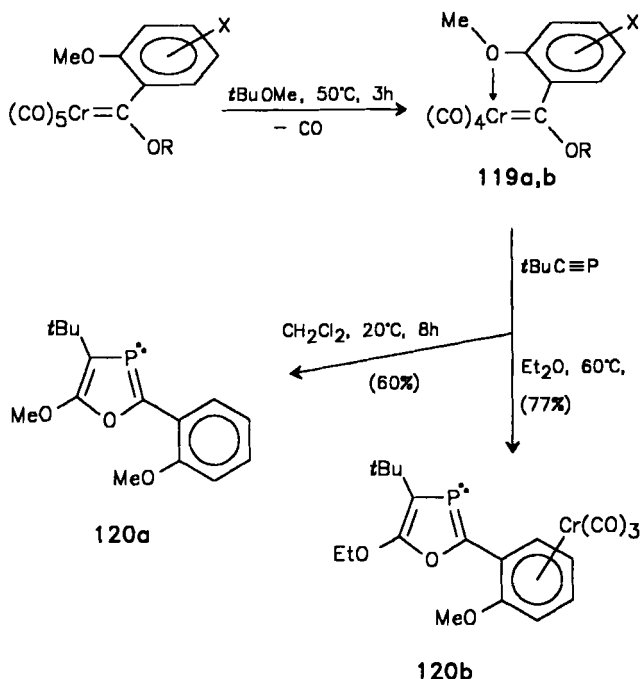
The reaction of $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)$ and $t\text{-BuC}\equiv\text{P}$ affords the dinuclear molybdenum complex **118**, featuring an $\eta^1:\eta^4$ -triphosphete ring in addition to an $\eta^1:\eta^4$ -1,3-diphosphete ligand, albeit in poor yield; see Eq. (26).^{56d}



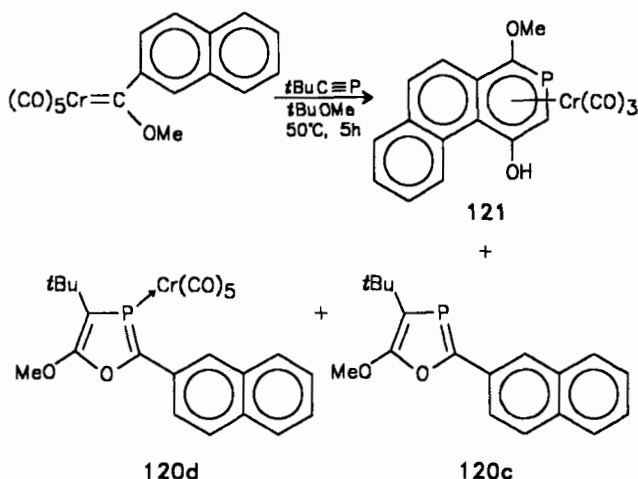
C. Five-Membered Rings

1,3-Oxaphospholes are produced in a chromium-mediated cocyclization of carbenes, carbon monoxide, and phosphalkynes. Thus, treatment of the carbene chelates **119a,b** with $t\text{-BuC}\equiv\text{P}$ leads to 1,3-oxaphospholes **120a,b** as the sole products (Scheme 31).⁵³ As already depicted in Scheme 26, (*Z*)-configured phosphalkenylketene–chromium complexes are invoked as intermediates in this transformation. Depending upon the substitution pattern at the carbene ligand, chromium-mediated annulation giving phosphaaerenes may seriously compete with the 1,3-oxaphosphole synthesis described here. In line with this, a 2-naphthylcarbene chromium complex and the phosphalkyne undergo reaction to yield a 1:1 mixture of 1,3-oxaphospholes **120c,d** and phosphaphenanthrene **121** (Scheme 32).⁵³ This annulation reaction, as well as the 1,3-oxaphosphole synthesis, have precedents in the chromium–carbene-mediated generation of hydroquinones and furanes involving alkynes instead of phosphalkynes.⁶¹

As already indicated in Eq. (19), cocondensation of metal atoms in a metal-vapor synthesis is a powerful tool for the generation of sandwich

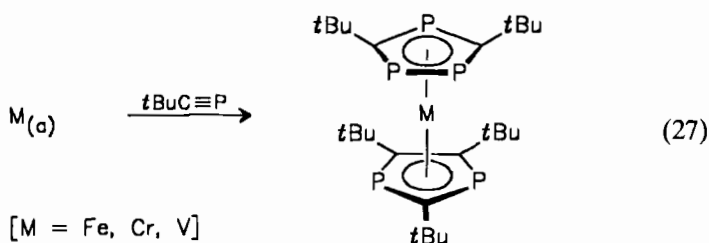


SCHEME 31.



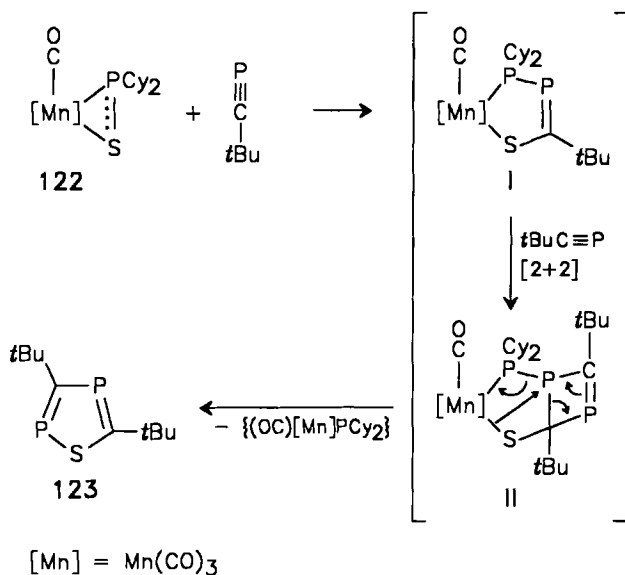
SCHEME 32.

complexes with phosphorus-containing π -ligands. Exposure of $t\text{-BuC}\equiv\text{P}$ to iron, chromium, or vanadium atoms affords heterometalloenes featuring η^5 -1,3-diphospholyl and 1,2,4-triphospholyl ligands, as shown in Eq. (27).^{50,62}



A great variety of π -complexes exhibiting di- and triphospholyl ligands are accessible by the reaction of a mixture of the alkali di- and triphospholides, as obtained from $t\text{-BuC}\equiv\text{P}$ and sodium or $\text{LiP}(\text{SiMe}_3)_2$, with the respective metal halides.^{3,50} The scope of this approach is, however, limited, and in some cases, oxidative coupling of these reagents accounts for cage formation.^{63,64}

It has been demonstrated that the $[\text{R}_2\text{PS}]$ -unit in thiaphospha-metallacyclopropanes behaves like an η^2 -heteroalkyne ligand, mainly because of similar covalent radii and comparable electronegativities of the phosphorus and sulfur atoms. This functionality therefore seems appropriate for metal-mediated cyclo-cotrimerizations with alkynes and phosphalkynes. Consistent with this premise, the 1-thia-2,4-diphosphole **123** is obtained in high

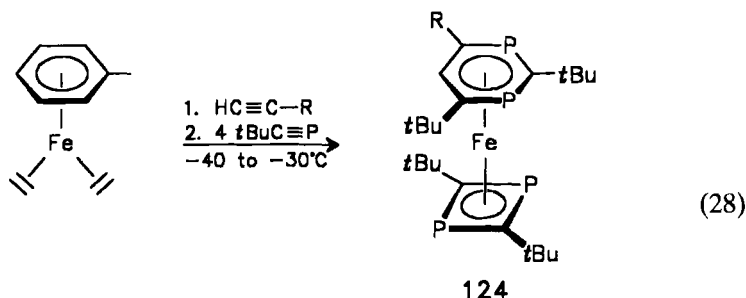


SCHEME 33.

yields from the (η^2 -thiophosphinito)manganese complex **122a** and 2 eq $t\text{-BuC}\equiv\text{P}$ (Scheme 33).³⁵ This transformation is explained by the insertion of the phosphalkyne into the $\text{P}-\text{S}$ bond of **122a** to give intermediate **I**. With sterically congested nickel complexes such as $\text{CpNi}(\eta^2\text{-R}_2\text{PS})$ ($\text{R} = m\text{-Xyl, Mes}$) as precursors and $t\text{-BuC}\equiv\text{P}$ the resulting insertion products of type **I** are stable. The decreased steric requirements in the case of the manganese derivative **I** allows the $[2+2]$ cycloaddition with a second molecule of $t\text{-BuC}\equiv\text{P}$ to transient **II**, which spontaneously releases **123**.³⁵ Similarly, **123** is obtained from the reaction of $(\text{Ph}_3\text{P})(\text{CO})_2\text{Co}(\eta^2\text{-Et}_2\text{PS})$ with an excess of $t\text{-BuC}\equiv\text{P}$.³⁶

D. Six-Membered Rings

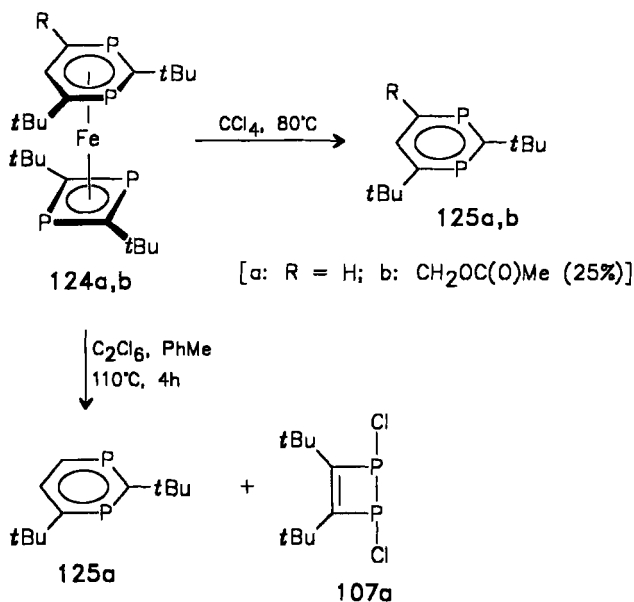
A stereospecific cyclo-cotrimerization of a terminal alkyne and two molecules of $t\text{-BuC}\equiv\text{P}$ to yield the η^6 -1,3-diphosphinine complexes **124** is achieved by reacting $\text{Fe}(\eta^6\text{-toluene})(\eta^2\text{-C}_2\text{H}_4)_2$ with the alkynes at -40°C to -30°C and exposing the mixture obtained to an excess of the phosphalkyne, see Eq. (28).⁶⁵



[a: R = H (55%); b: CH₂OC(O)Me (35%); c: *n*Bu (40%);
d: CH₂OH (35%); e: CH₂OMe (35%)]

The reaction fails with 3,3-dimethylbutyne and internal alkynes, whereas functionalities such as hydroxy, ether, or ester groups are tolerated.

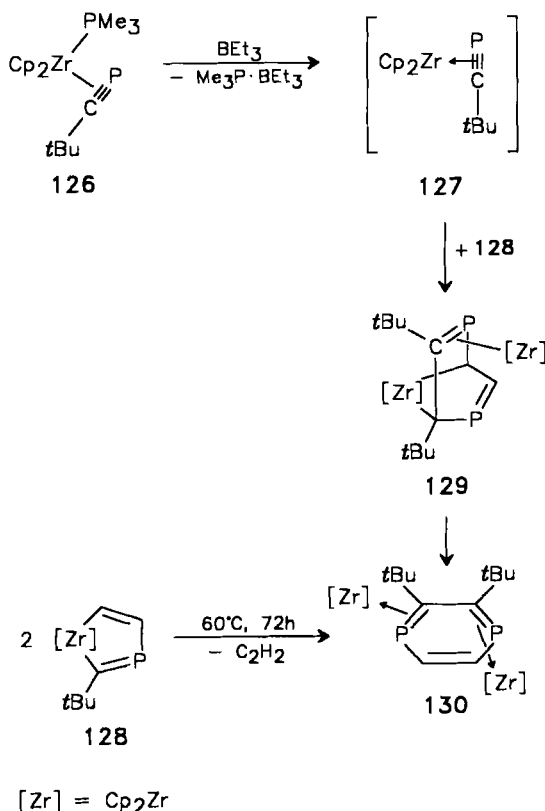
The oxidative decomplexation of the 1,3-diphenylphosphinines **125a,b** from **124a,b** is accomplished in boiling CCl₄.⁶⁵ The oxidation of **124a** with C₂Cl₆ in refluxing toluene, however, leads to the release of both organophosphorus ligands. By this means, the 1,3-diphenylphosphite is converted into **107a** (Scheme 34).^{57c} The dark-red microcrystalline (1,4-diphenylphosphine)dizirconium complex **130** forms almost quantitatively, when an equimolar mixture of the (η²-phosphaalkyne)zirconium complex **126**, 1-phospha-3-zirconiacyclopent-



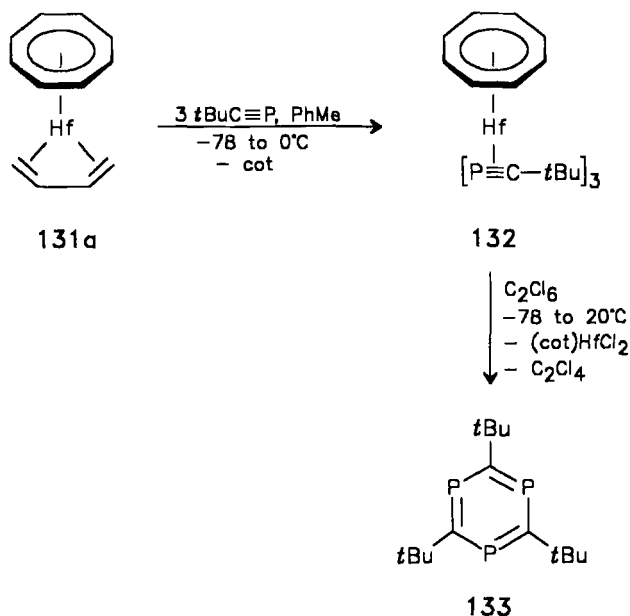
SCHEME 34.

tadiene **128**, and BEt_3 is warmed in toluene from -78 to 20°C (Scheme 35).⁶⁶ Complex **128** is pregenerated from **126**, BEt_3 , and acetylene. Accordingly, thermolysis of **128** also furnishes the 1,4-diphosphinine species in high yield. The key step of the reaction is believed to be a Diels–Alder addition of the heterocyclopentadiene **128** to the η^2 -ligated phosphalkyne in the transient species **127**.⁶⁶

The first 1,3,5-triphosphinine **133** with only two-coordinate phosphorus atoms is produced by the hafnium-mediated cyclotrimerization of $t\text{-BuC}\equiv\text{P}$ in toluene at -78°C and the subsequent release of **133** from **132** by oxidation with hexachloroethane in toluene in the range -78 to 20°C (Scheme 36).⁶⁷ Low temperatures are crucial for the generation of hafnium complexes with ligated cyclotrimers of the phosphalkyne. At 140°C , cyclodimerization to give $(\text{cot})(\eta^4\text{-1,3-diphosphete})\text{hafnium}$ is observed, whereas



SCHEME 35.



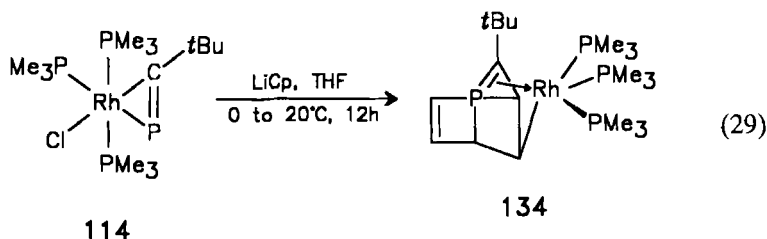
SCHEME 36.

at room temperature, metal-assisted cyclotetramerization of $t\text{-BuC}\equiv\text{P}$ takes place (vide infra).

Obviously, the 12-valence-electron fragment $[\text{Hf}(\eta^8\text{-cot})]$, which forms by loss of butadiene, is an ideal template for the accommodation of more than two phosphalkyne molecules. As illustrated later, the 14-electron fragment $[\text{HfCp}_2]$ only allows cyclodimerization of phosphalkynes, and similar observations have been made with electron-rich transition metals such as Ni, Co, Rh, and Fe.

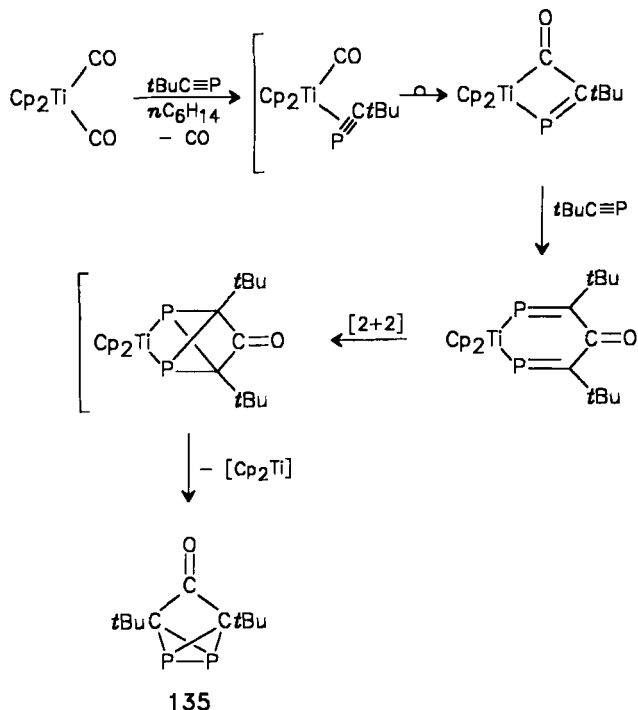
E. Polycyclic Compounds and Cages

An excellent review has discussed the synthesis of organophosphorus cages employing phosphalkynes as precursors.⁶⁸ In order to avoid unnecessary duplication of coverage, the results here reported are restricted to transition-metal-assisted transformations. An intramolecular $[2+4]$ cycloaddition between an η^2 -phosphalkyne and an η^1 -cyclopentadienylligand to yield compound **134** is observed during the reaction of complex **114** with lithium cyclopentadienide, as shown in Eq. (29).^{56c}



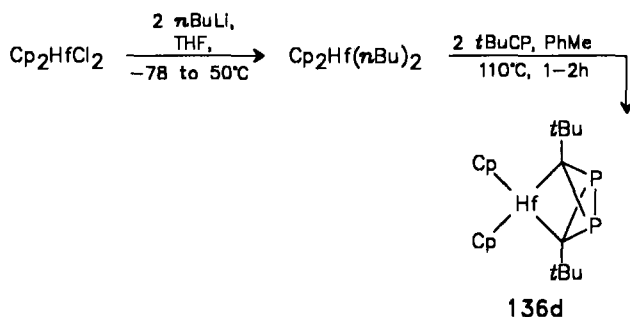
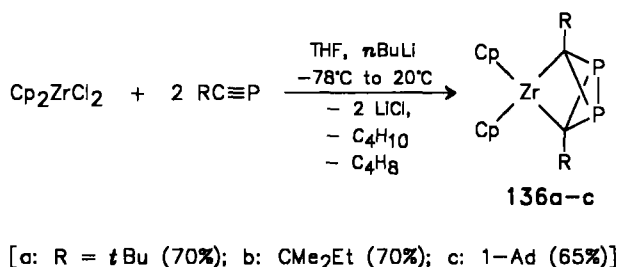
Two molecules of *t*-BuC≡P and one carbon monoxide ligand combine to give the cage molecule **135** upon cothermolysis of Ti(CO)₂Cp₂ and the phosphalkyne in boiling *n*-hexane (Scheme 37).⁶⁹

A 1,3-diphosphabicyclo[1.1.0]butanediyl ligand chelating a zirconium or hafnium center results from the reaction of MCl₂Cp₂ (M = Zr, Hf) with two molar equivalents of *n*-butyllithium at −78°C, and treatment of intermediate M(*n*-Bu)₂Cp₂ with two molecules of phosphalkyne. The formation of the yellow to red crystalline zirconium derivatives **136a–c** is accomplished at room temperature,^{70a} whereas heating in toluene at 110°C is needed to

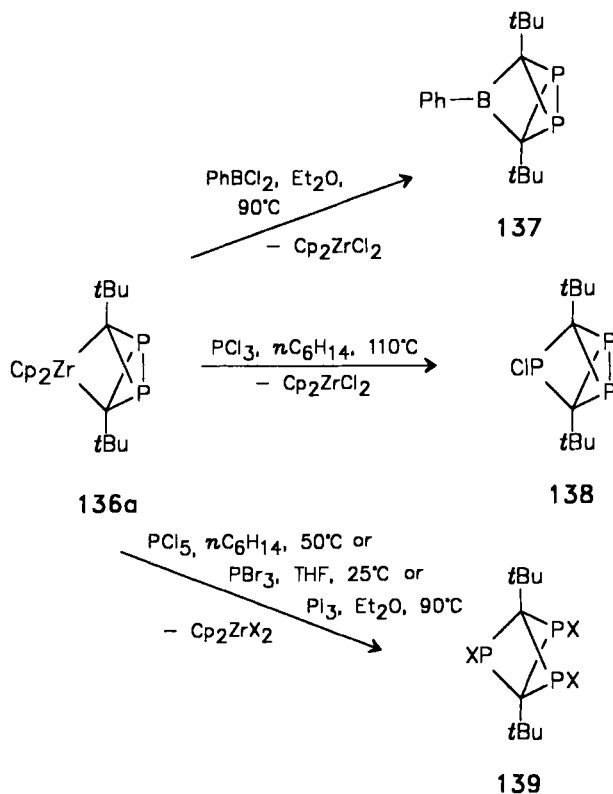


SCHEME 37.

afford the orange-red hafnium analog **136d**^{70b} (Scheme 38). In contrast with the majority of η^4 -1,3-dihydrophosphete metal complexes (M = Fe, Co, Rh, Ni), where the removal of the organophosphorus ligand fails, complexes **136a,d** are valuable and convenient sources for a number of phosphorus heterocycles (Scheme 39).^{70b,71} Heating **136a** with PhBCl₂ in a pressure tube leads to the exchange of the [ZrCp₂] fragment by a [PhB] unit to produce cage **137**. The tricyclic framework is sustained when **136a** is subjected to reaction with phosphorus trichloride in a similar vessel. In contrast to this, treatment of **136a** with PBr₃ or PI₃ leads to replacement of the [ZrCp₂] group and cleavage of the P—P bond with formation of the bicyclic species **139b,c**. The corresponding chloro derivative **139a** results from the reaction of **136a** with PCl₅ in *n*-hexane at 90°C. The cleavage of the Zr—C bonds in **136a** with HgCl₂ or bromine at -78°C is accompanied by complete degradation of the polycyclic structure and generation of 1,3-diphosphetanes **140a,b**. The hydrogen atoms in the 2,4-positions of the ring have presumably been abstracted from the solvent, which points to a radical mechanism (Scheme 40).⁷¹ In contrast with this, complex **136a** is oxidized by 2 eq iodine to afford 1,2-diiodo-1,2-diphosphete **107c**. A *cis/trans* mixture



SCHEME 38.

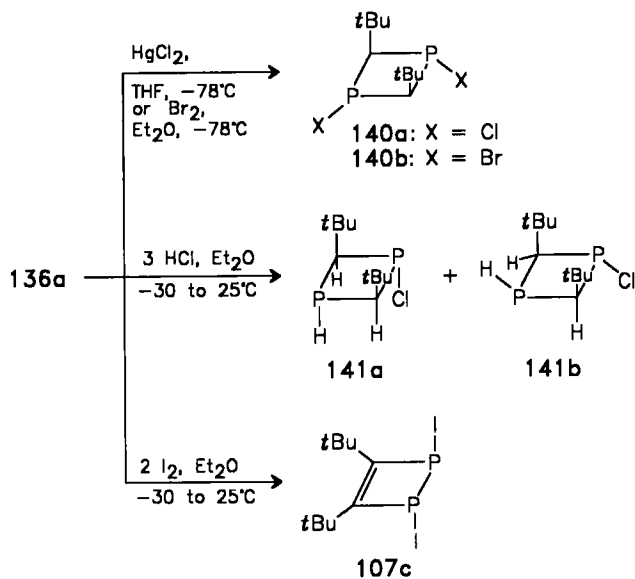


[a: X = Cl; b: Br; c: I]

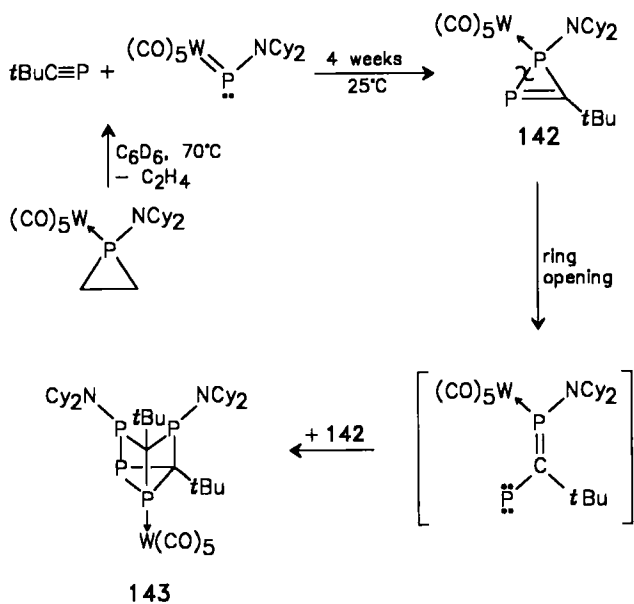
SCHEME 39.

(1:2) of the 1,3-diphosphetanes **141a** and **141b** is obtained upon exposure of **136a** to hydrogen chloride (Scheme 40).⁷¹

The 1-H-diphosphirene complex **142**, generated thermally by [2+1] cycloaddition of a short-lived phosphinidene complex to $t\text{-BuC}\equiv\text{P}$, undergoes dimerization with elimination of one $[\text{W}(\text{CO})_5]$ unit to afford the tricyclopophosphahexane **143**. The cage framework is constructed from two phosphalkyne and two phosphinidene building blocks. Ring opening of transient **142** and the [2+1] cycloaddition of the resulting phosphinidene to the $\text{P}=\text{C}$ bond of a second molecule of **142** is considered the key step in this transformation (Scheme 41).⁷² A number of different polycyclic ligands, including three phosphalkyne units, can be synthesized in the coordination sphere of metals. In Scheme 38 the construction of 1,3-diphosphabicyclo[1.1.0]butanediyl-zirconocenes and -hafnocenes is illustrated. An analogous reaction sequence starting with TiCl_2Cp_2 is much more compli-

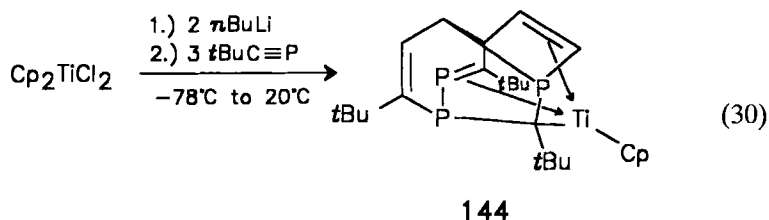


SCHEME 40.



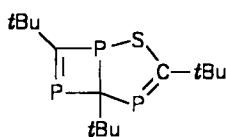
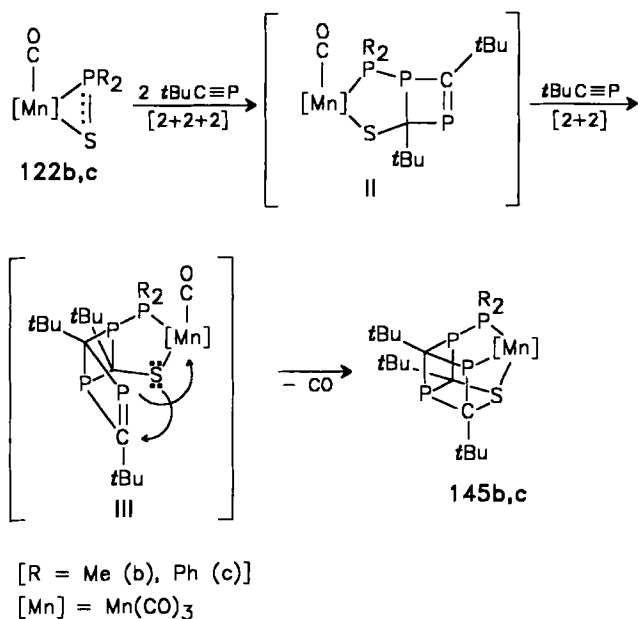
SCHEME 41.

cated and incorporation of one cyclopentadienyl ligand into product **144** is encountered; see Eq. (30).⁷³



As shown in Scheme 33, cotrimerization of a sulfur atom and two phosphalkyne molecules is possible.

Reduction of the size of the substituents at the thiophosphinito ligand in **122** changes the reactivity of the manganese complex towards phosphalkynes markedly (Scheme 42). With R = Me, a third molecule of *t*-BuC≡P



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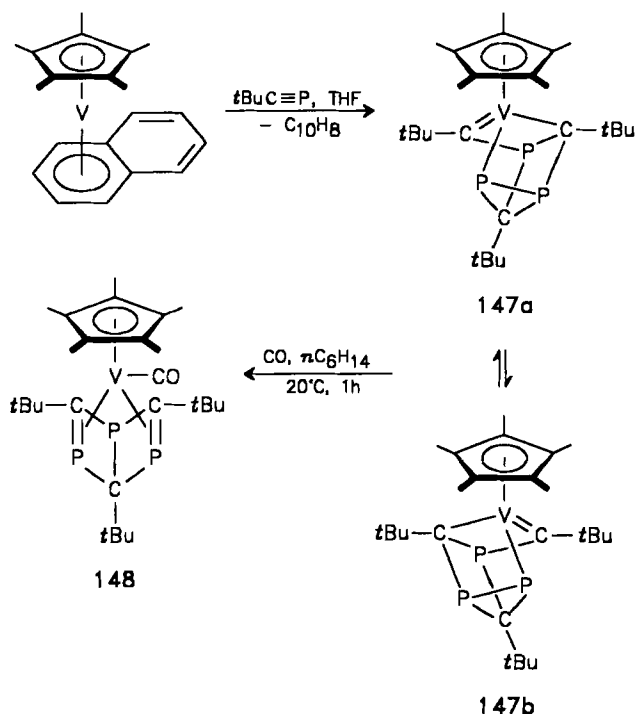
SCHEME 42.

is added to the bicyclic intermediate **II**, yielding transient **III**, which rearranges to cage complex **145b** by a [2+2] cycloaddition of the [Mn-S] unit to the P=C bond (Scheme 42).³⁵

Commencing with **122c** (R = Ph), the steric requirement of the precursor is between that of **122a** (R = Cy) and **122b** (R = Me). Consistent with this, the generation of the 1,2,4-thiadiphosphole **123** is accompanied by the pentacycle **145c** (R = Ph) and the metal-free yellow bicyclic compound **146**.³⁵

The first metal-induced cyclotrimerization of a phosphalkyne was realized within the coordination sphere of vanadium. The exothermic reaction of $t\text{-BuC}\equiv\text{P}$ with $\text{Cp}^*(\eta^6\text{-naphthalene})\text{vanadium}$ furnishes the dark-brown crystalline organovanadium complex **147**, which displays a fluxionality (Scheme 43).⁷⁴ At ambient temperatures, compound **147** smoothly adds one molecule of CO to give the dark-green $\eta^4\text{-Dewar 1,3,5-triphosphabenzene}$ complex **148**.⁷⁴

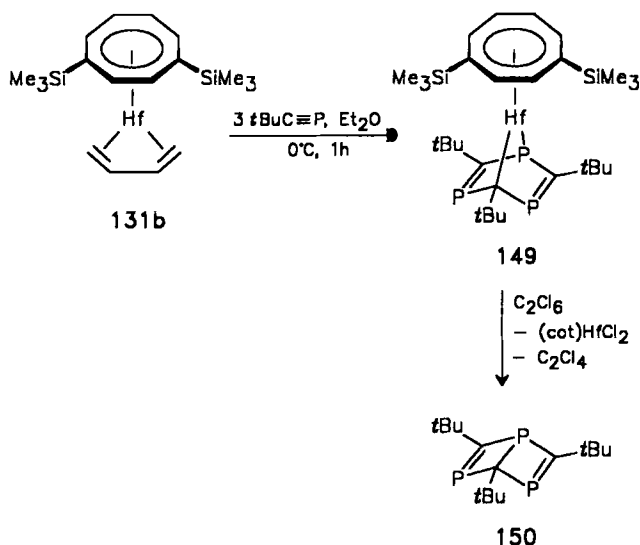
The products obtained in the reaction of the cyclooctatetraene hafnium complex with phosphalkynes are temperature-controlled. If **131b** is treated with $t\text{-BuC}\equiv\text{P}$ at 0°C, three molar equivalents of the phosphalkyne are



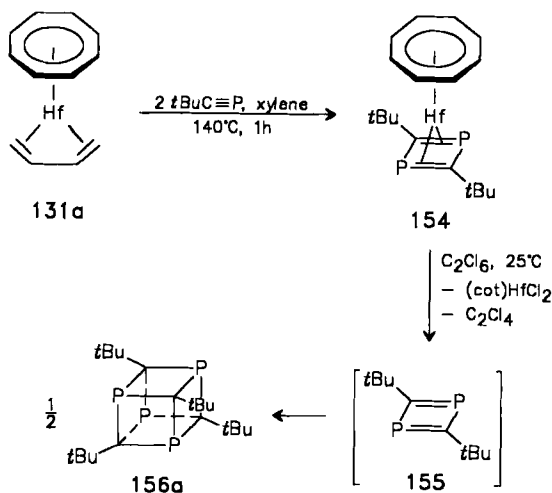
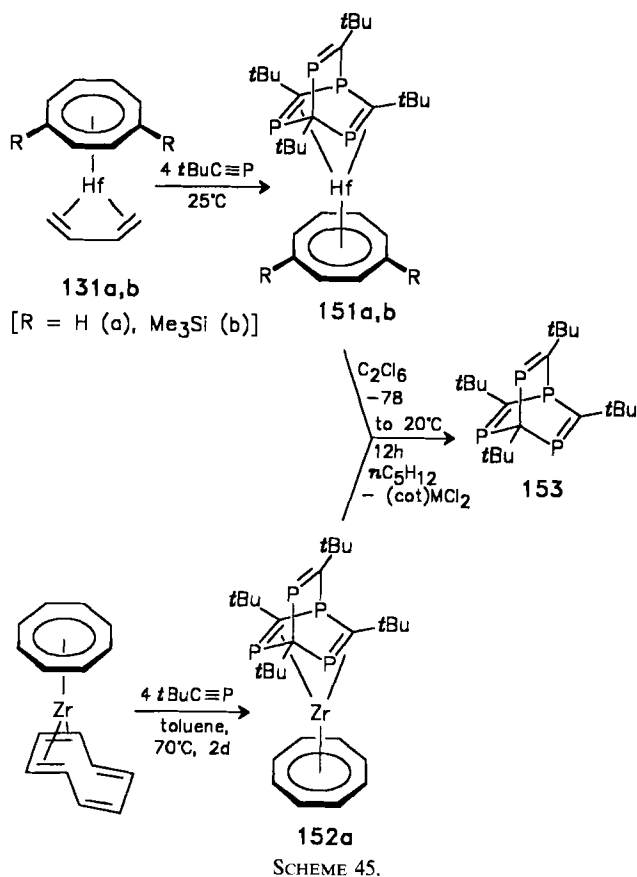
SCHEME 43.

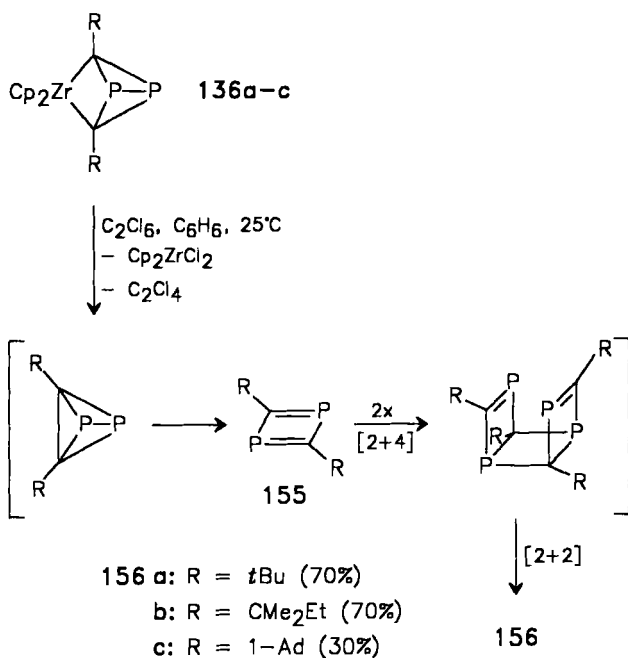
accommodated at the metal center to give complex **149**. The proposed structure of the molecule is chemically supported by the cleavage of the orange microcrystalline Dewar 1,3,5-triphosphabenzene **150** with C_2Cl_6 (Scheme 44).⁶⁷ Raising the temperature of this reaction to 25°C leads to the cyclotetramerization of the phosphaaalkyne with quantitative formation of the tetraphosphabarralene complexes **151a,b**. The zirconium analog **152b** is also obtained under these conditions. However, for the synthesis of the tetraphosphabarralenezirconium complex **152a** from $\text{Zr}(\text{cot})_2$ and 4 eq $t\text{-BuC}\equiv\text{P}$ heating to 70°C is necessary. Release of the yellow, crystalline 1,3,5,7-tetraphosphabarralene **153** from complexes **151** or **152** is effected by oxidation with C_2Cl_6 (Scheme 45).⁷⁵

If the reaction of **131a** with $t\text{-BuC}\equiv\text{P}$ is performed in boiling xylene (140°C), the brown complex **154**, featuring a 1,3-diphosphete ligand, is isolated in 68% yield.⁶⁷ From ^{31}P and ^{13}C NMR evidence, it is suggested that the π -electrons in the η^4 -ligated 1,3-diphosphete are not completely delocalized as given in the corresponding complexes of Co, Rh, or Fe. This assumption is confirmed by an X-ray analysis of **154**, where alternation of the P—C bond lengths (1.748 and 1.828\AA) is encountered.⁶⁷ Diphosphete **155** is split off from **154** by chlorination with C_2Cl_6 at ambient temperature. As expected, **155** is not sufficiently stable to be isolated or detected spectroscopically. The only isolable product is the tetraphosphacubane **156a** (34% yield), which is derived from **155** by a sequence of [4+2] and [2+2] cycloadditions (Scheme 46). Alternative methods for the



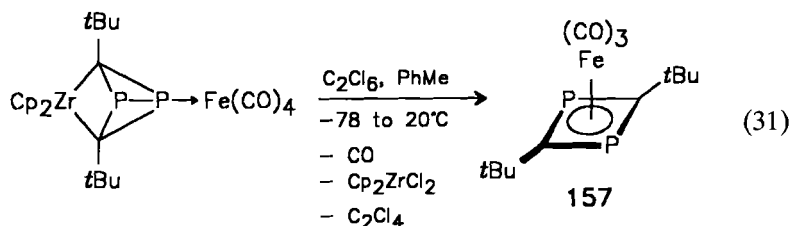
SCHEME 44.





SCHEME 47.

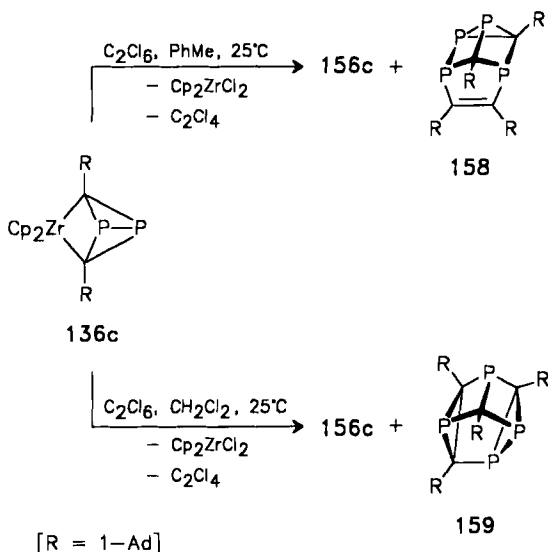
conversion of *t*-BuC≡P into the cubane-type cage **156a** are based upon prolonged heating of the phosphalkyne at 130°C⁷⁶ or exposure to CH₂(AsCl₂)₂ at ambient temperature.⁷⁷ Clearly, the oxidative degradation of the zirconium complexes **136a-c** by C₂Cl₆ provides the most effective access to tetraphosphacubanes **156a-c** (Scheme 47).^{70a} Again, the dimerization of transient 1,3-diphosphete **155** is regarded as the key step of cage formation. In keeping with this, the transient diphosphete is intercepted as a ligand in the iron complex **157**, provided that the chlorination is performed with the tetracarbonyliron adduct of **136a**; see Eq. (31).^{70a}



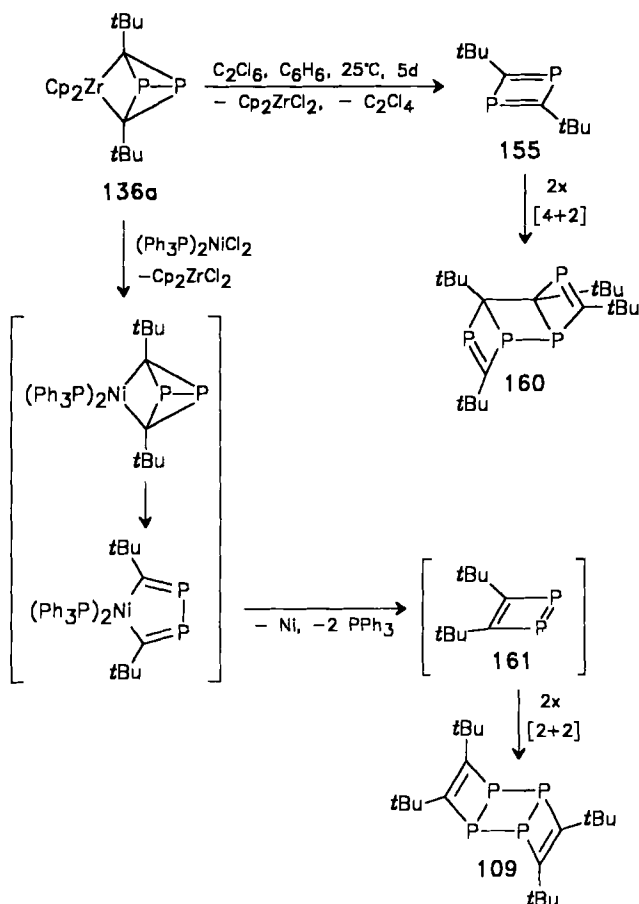
The synthesis of tetraphosphacubane **156c** ($R = 1\text{-Ad}$) in toluene is accompanied by the generation of an equal amount of the isomeric tetraphosphabis(homo)prismane **158**. In the more polar solvent CH_2Cl_2 , the oxidative cleavage of **136c** leads to a 1:1 mixture of **156c** and tetraphosphacuneane **159** (Scheme 48).⁶⁸ During the synthesis of tetraphosphacubane **156a**, a few orange-red rods were formed, and they were separated by hand from the principal product and identified as the tricyclic cyclotetramer **160** of the phosphaaalkyne (1% yield).

The isomeric tricycle **109** results from the attempted transfer of the organophosphorus ligand from zirconium onto nickel (70%) (Scheme 49). The intermediacy of the anticipated nickel complex is likely. Its isomerization and decomposition yields 1,2-diphosphete **161**, which dimerized to the observed product.⁷⁸ As shown earlier, in Eqs. (20) and (25) and Scheme 41, the reactivity of phosphinidine tungsten complexes towards phosphaaalkynes is governed by the substituents in both components. Accordingly, red crystalline pentaphosphadeltacyclanes **166a,b** are obtained by thermolysis (90°C) of the phosphirane complex **162** in the presence of a 7–10-fold excess of the phosphaaalkynes (Scheme 50). Four phosphaaalkyne building blocks are incorporated in the tetracyclic skeleton of the products.⁷⁹

It is conceivable that this transformation is initiated by a $[2+1]$ cycloaddition of a transient phosphinidene complex with the phosphaaalkyne to give the $2H$ -diphosphirene derivative **163**. Ring opening and the subsequent



SCHEME 48.

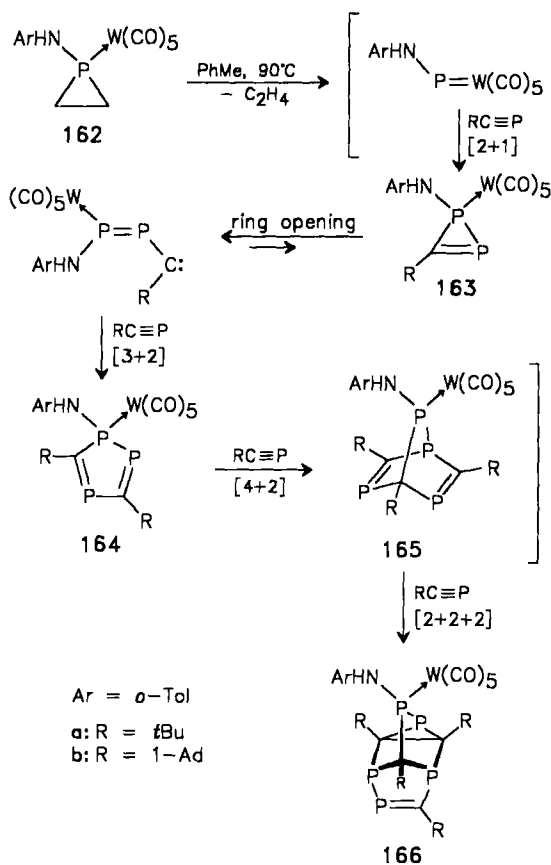


SCHEME 49.

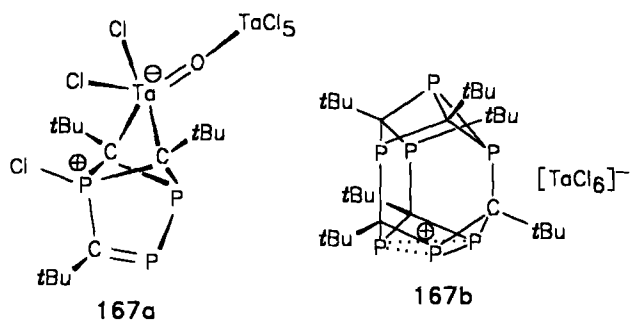
$[3+2]$ cycloaddition of the resulting carbene to a second molecule of $\text{RC}\equiv\text{P}$ furnishes the triphosphole **164**, which adds to a third equivalent of phosphaaalkyne in a Diels–Alder reaction. Transient tetraphosphanorbornadiene **165** is finally trapped by $\text{RC}\equiv\text{P}$ in a $[2+2+2]$ cycloaddition to give **166**.⁷⁹

The tricyclic zwitterion **167a** and the salt **167b**, containing a heptacyclic organophosphorus cation, are isolated from the reaction between $t\text{-BuC}\equiv\text{P}$ and TaCl_5 in CH_2Cl_2 . In the cation, six molecules of phosphaaalkyne are combined.⁸⁰ (See Formula 1.)

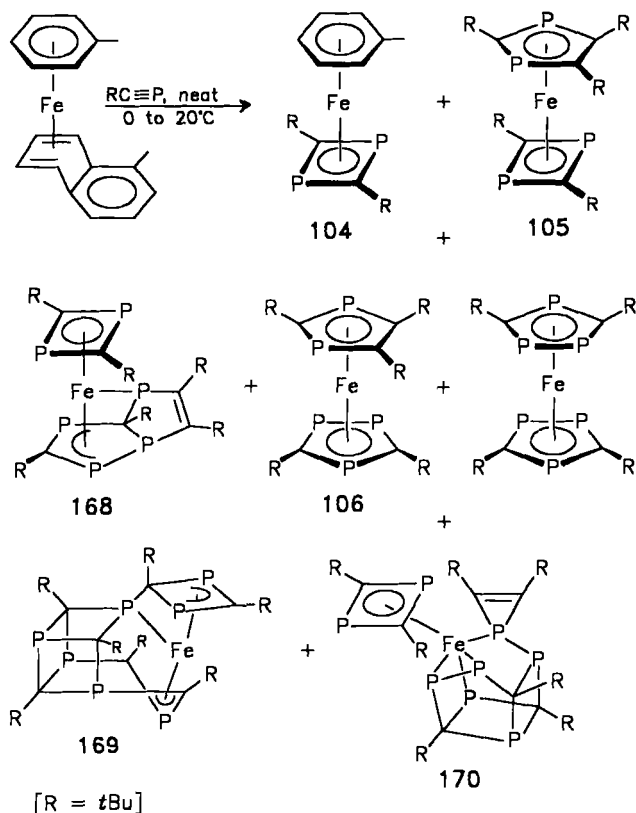
Reacting $(\eta^6\text{-toluene})(\eta^4\text{-1-methylnaphthalene})\text{iron}$ with a 20-fold excess of neat $t\text{-BuC}\equiv\text{P}$ in the temperature range 0 to 20°C affords small amounts of the iron-containing cage compounds **168–172**. In addition to this, a



SCHEME 50.



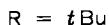
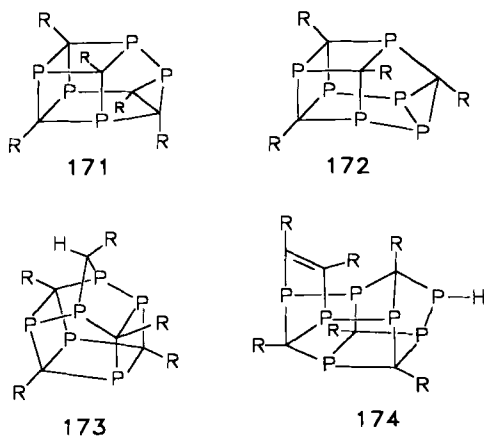
FORMULA 1.



SCHEME 51.

number of sandwich complexes are obtained. (See Scheme 51.) The two paramagnetic molecules **168** and **169** are composed of six or seven phosphalkyne units, whereas **170** exhibits one more phosphorus and hydrogen atom in addition to the seven $\text{RC}\equiv\text{P}$ building blocks. All three complexes display a 1,3-diphosphaalkyne moiety in combination with a bicyclic phosphalkyne tetramer (**168**), a partly opened pentameric cage (**169**), or the pentaprism-like skeleton in **170**.⁸¹ The yield of **168** can be improved to 24% by exposure of $\text{Fe}(\eta^6\text{-toluene})(\text{C}_2\text{H}_4)_2$ to an 11-fold excess of $t\text{-BuC}\equiv\text{P}$.

When the reaction mixture, as given in Scheme 51, is heated to 100°C for an hour before workup, the metal-free cages **171–174** can be separated by medium-performance liquid chromatography (MPLC).⁸² (See Formula 2.) Formally, compound **171** is derived from tetraphosphacubane **156a** by addition of a fifth equivalent of $t\text{-BuC}\equiv\text{P}$, and **172** results from the cubane by incorporating one P_2 unit. Cages **173** and **174** are constructed from five



FORMULA 2.

or six phosphalkyne building blocks in addition to an extra phosphorus and a hydrogen atom. A alternative pathway to the pentamer **171** involves the oxidative coupling of the 1,3-diphospholyl and 1,2,4-triphospholyl anions with $FeCl_3$.^{63b}

VI

CONCLUSIONS AND PROSPECTS

What have we learned? First, that we should not consider rules, models, and concepts as established dogmas, but rather regard them as anthropogenic attempts to rationalize observations, knowledge, and experience. Here, however, it is crucial to define cleanly the scope and the limitation of the respective rule (or model or concept). Obviously, in the case of the classical view of double-bond formation important points have been overlooked. Phosphaalkenes and phosphalkynes, once regarded as "non-existent molecules," are now well-known and well-respected members in the steadily growing family of organophosphorus compounds, and they display a rich and multifarious chemistry. The employment of transition-metal complexes in chemical transformations with the species under discussion benefits from various advantages: (i) stabilization of reactive precursors and intermediates; (ii) a stereochemically appropriate accommodation of reactants at the metal-center template; and (iii) activation of PC multiple bonds by ligation. These advantages are prerequisites for the synthesis of

the plethora of novel ring and cage compounds described in this chapter. Moreover, the concepts of diagonal C/P relationship in the periodical table and of isoelectronic compounds point to a close relationship between organic and phosphorus chemistry and, of course, the domain of organophosphorus chemistry. The types of reactions and structures discussed herein provide many examples in impressive support of these ideas.

This research area is continuously growing. It is evident that small changes of the ligands or at the metal centers in a given transition-metal complex often lead to different products. Bearing in mind the rich coordination chemistry displayed by *d*-block elements, one concludes that transition-metal-assisted syntheses with phosphalkenes and -alkynes will persist as a highly prolific research area.

VII

ABBREVIATIONS USED IN THIS REVIEW

Ad	adamantyl
Ar	aryl
bpy	2,2'-bipyridine
Bu	butyl
coc	(<i>Z</i>)-cyclooctene
cod	cycloocta-1,5-diene
cot	cyclooctatetraene
Cy	cyclohexyl
Cp	$\eta^5\text{-C}_5\text{H}_5$
Cp*	$\eta^5\text{-C}_5\text{Me}_5$
dmb	2,3-dimethyl-1,3-butadiene
dme	1,2-dimethoxyethane
dppe	1,2-bis(diphenylphosphino)ethane
Et	ethyl
Ind	indenyl
Me	methyl
Mes	mesityl (2,4,6-Me ₃ C ₆ H ₂)
Mes*	supermesityl (2,4,6- <i>t</i> Bu ₃ C ₆ H ₂)
Ph	phenyl
Pr	propyl
Py	pyridine
Tol	tolyl
Xyl	xylyl

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Synthesis and Reactions of Polynuclear Cobalt–Alkyne Complexes

MICHAEL J. WENT

Department of Chemistry
University of Kent
Canterbury, Kent
CT2 7NH, United Kingdom

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I

INTRODUCTION

In 1974, Dickson and Fraser reviewed the already substantial area of cobalt–alkyne complexes.¹ Since then the number of examples and applications of this class of organometallic compounds, especially dinuclear complexes, has increased enormously. This review will present the chemistry of polynuclear cobalt–alkyne complexes, with emphasis on the more recent developments. Although there have been many exciting fundamental discoveries, this is a maturing area of research that is finding many important applications in organic synthesis,² such as the use of $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ complexes in the synthesis of enediyne antitumor antibiotics.^{3,4}

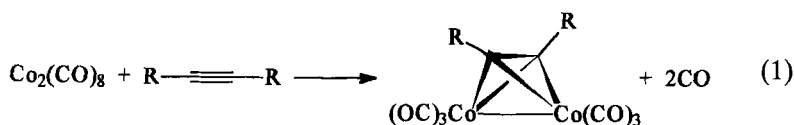
II

DINUCLEAR COMPLEXES

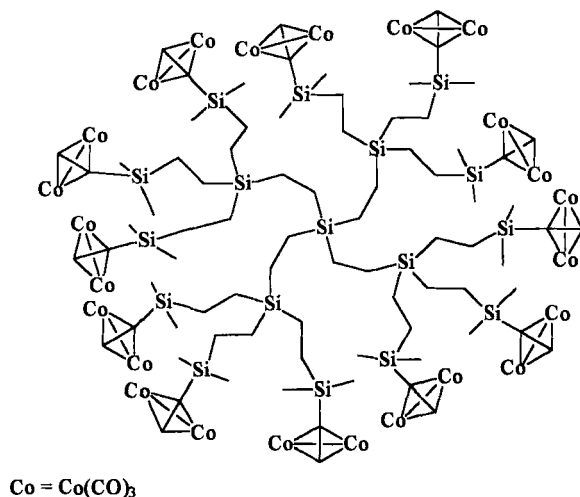
A. Synthesis

Although many metal–alkyne complexes are known, probably the most thoroughly studied are those in which the alkyne is coordinated with a dicobalt unit. When this area was reviewed in 1974, more than 170 examples

were known, and many hundreds of new complexes have been described since then.¹ The driving force for such intense investigation is the applications of these compounds in organic synthesis, while the development of the chemistry and applications of dicobalt–alkyne complexes are greatly facilitated by the easy synthesis of hexacarbonylalkyne–dicobalt complexes. Octacarbonyldicobalt reacts readily in organic solvents at room temperature with a large range of alkynes to yield compounds of the general formula $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$, as shown in Eq. (1).¹



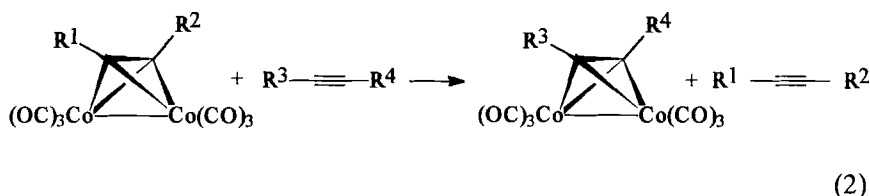
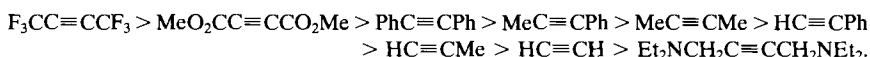
Typically, the hexacarbonylalkyne–dicobalt complexes are dark red liquids or solids that are easily purified by crystallization or chromatography and can be stored in air for long periods of time.¹ The reaction is general and has been demonstrated with virtually every conceivable alkyne, including terminal alkynes, symmetrically and unsymmetrically substituted alkynes containing carbon, arsenic, phosphorus, silicon or transition metal centers *alpha* to the alkyne functionality, and diynes, triynes, poly-ynes, and cyclic alkynes. An example that illustrates the utility of this reaction is the preparation of carbosilane dendrimer **1** (see Formula 1), containing 12 peripheral hexacarbonylalkyne–dicobalt substituents, via the reaction of $\text{Si}(\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{C}\equiv\text{CH})_3)_4$ with octacarbonyldicobalt.⁵



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FORMULA 1.

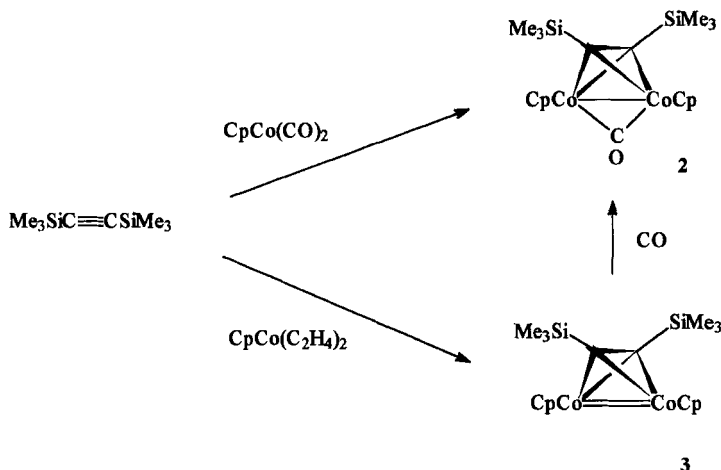
Only severely sterically hindered alkynes, such as $[(OC)_9Co_3CC\equiv CC Co_3(CO)_9]$,⁶ fail to react with octacarbonyldicobalt. This steric effect is also illustrated by the reactions of $[Cp(OC)_2FePPh_2C\equiv CR]^+$ ($R = H, Me, Ph, p\text{-tolyl}, t\text{-Bu}$) with octacarbonyldicobalt.⁷ All of the cationic alkyne complexes form hexacarbonylalkyne-dicobalt derivatives except when the substituent is the bulky *t*-Bu group.

The $[Co_2(\mu\text{-alkyne})(CO)_6]$ complexes themselves can act as precursors to further complexes of this type via treatment with alkynes bearing more electronegative substituents which form hexacarbonylalkyne-dicobalt complexes of greater stability $[Eq. (2)]$ ^{8a} although the reproducibility of this reaction has been questioned.^{8b} Displacement is reported to take place in the following order:



It is also possible to release the alkyne from $[Co_2(\mu\text{-alkyne})(CO)_6]$ complexes with oxidizing reagents such as Ce(IV), Fe(III), and amine *N*-oxides.⁹ This has given rise to applications in protecting the alkyne functionality and allows the release of products after transformation at a remote functional group or a dicobalt-mediated transformation (see Section VI). Other preparative routes for $[Co_2(\mu\text{-alkyne})(CO)_6]$ complexes have been described,¹ but are of little general utility, with the exception of a recent report of an attractive alternative that avoids the use of octacarbonyldicobalt. Reduction of $CoBr_2$ in anhydrous THF with zinc dust in the presence of alkynes while CO is bubbled through the reaction mixture affords the corresponding alkyne complexes.¹⁰ The diphenylacetylene derivative, $[Co_2(\mu\text{-PhC}_2\text{Ph})(CO)_6]$, can be isolated in 85% yield by this method, and it has been demonstrated that a range of $[Co_2(\mu\text{-alkyne})(CO)_6]$ complexes can be prepared *in situ* before proceeding with a Pauson-Khand cyclization (see Section VI) with alkenes to afford cyclopentenones in yields comparable to those of the original procedures.

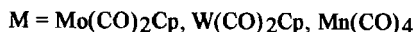
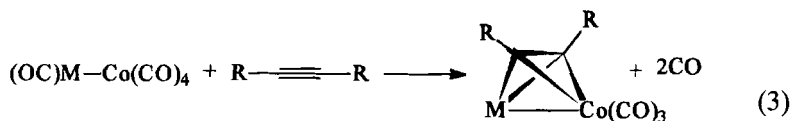
Reaction of $[Co(CO)_2Cp]$ with $Me_3SiC\equiv CSiMe_3$ in boiling xylene affords $[Co_2(\mu\text{-Me}_3SiC_2SiMe_3)(\mu\text{-CO})Cp_2]$ (2) in 93% yield.¹¹ Treatment of



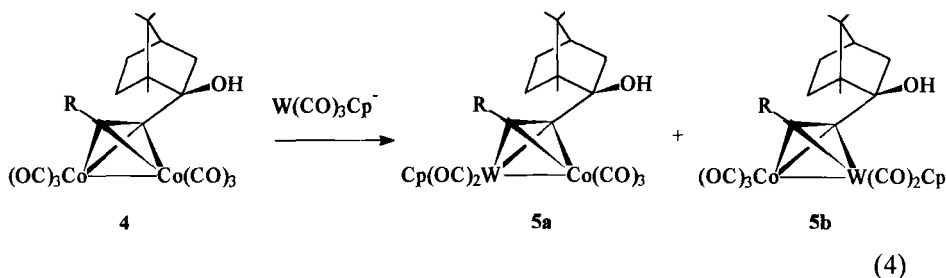
SCHEME 1.

$[\text{Co}(\text{C}_2\text{H}_4)_2\text{Cp}]$ with $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ at room temperature results in displacement of one ethene ligand and formation of the mononuclear complex $[\text{Co}(\text{C}_2\text{H}_4)(\text{Me}_3\text{SiC}_2\text{SiMe}_3)\text{Cp}]$. Attempts to isolate this complex by removal of the solvent under vacuum resulted in formation of the unsaturated air-sensitive dinuclear compound $[\text{Co}_2(\mu\text{-Me}_3\text{SiC}_2\text{SiMe}_3)\text{Cp}_2]$ (**3**) containing a cobalt–cobalt double bond.¹² Reaction of **3** with CO is extremely facile and produces **2** (Scheme 1).

Although heterobinuclear alkyne complexes have been less intensively studied, a number of routes involving cobalt as one of the metals have been developed. Compounds with two different metals are expected to have reactivity patterns different from those of the respective homonuclear species and also have applications in the preparation of chiral complexes. In a manner analogous to Eq. (1) the mixed-metal complexes $[\text{MCo}(\text{CO})_7\text{Cp}]$ ($\text{M} = \text{Mo}, \text{W}$) and $[\text{CoMn}(\text{CO})_9]$ react with a range of alkynes to afford complexes of the type $[\text{MCo}(\mu\text{-alkyne})(\text{CO})_5\text{Cp}]$ ^{13,14} and $[\text{CoMn}(\mu\text{-alkyne})(\text{CO})_7]$,¹⁵ as illustrated in Eq. (3).

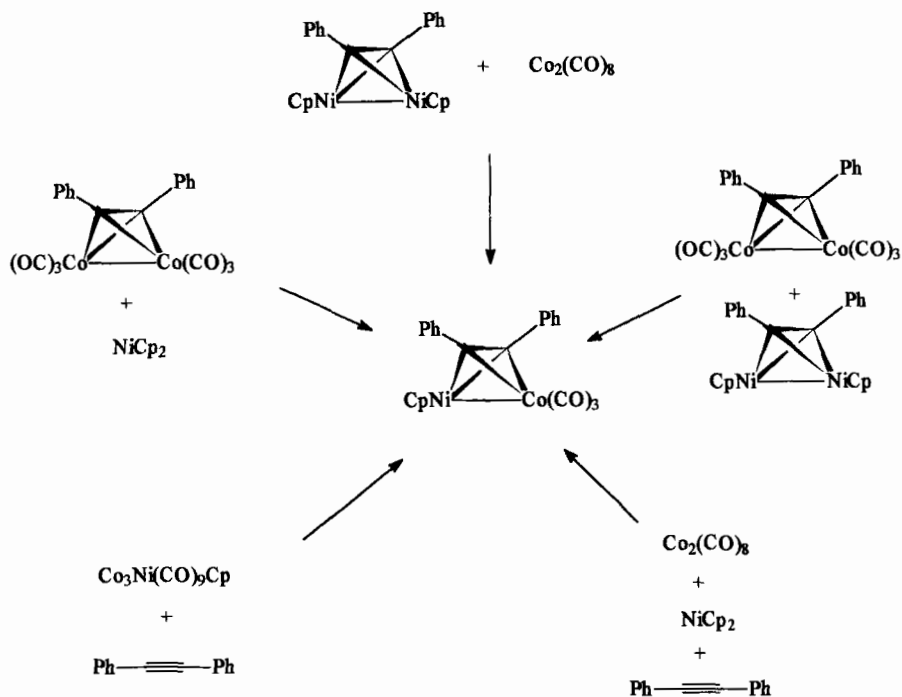


The complex $[\text{CoMo}(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{CO})_5\text{Cp}]$ can also be prepared by replacement of a $\text{Co}(\text{CO})_3$ fragment in $[\text{Co}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{CO})_6]$ by the isolobally related $\text{CpMo}(\text{CO})_2$ fragment. This can be effected by the benzo-phenoneketyl-initiated reaction of $[\text{Co}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{CO})_6]$ with $[\text{Mo}_2(\text{CO})_6\text{Cp}_2]$ or, more satisfactorily, by the thermal reaction of $[\text{Co}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{CO})_6]$ with the anion $[\text{Mo}(\text{CO})_3\text{Cp}]^-$.¹⁶ Vertex substitution using $[\text{M}(\text{CO})_3\text{L}]^-$ ($\text{M} = \text{Mo}$ or W ; $\text{L} = \text{Cp}$ or Cp') has been used in several other preparations, including alcohol-substituted complexes such as $[\text{MoCo}(\mu\text{-HOCH}_2\text{C}_2\text{CH}_2\text{OH})(\text{CO})_5\text{Cp}]$ from $[\text{Co}_2(\mu\text{-HOCH}_2\text{C}_2\text{CH}_2\text{OH})(\text{CO})_6]$ ¹⁷ and various molybdenum- or tungsten-cobalt complexes from enantiomerically pure menthyl- or bornyl-substituted dicobalt-alkyne complexes, which result in significant diastereoselectivity as determined by ^{13}C NMR spectroscopy.¹⁸ For example, treatment of **4** with $[\text{W}(\text{CO})_3\text{Cp}]^-$ gives a 75:25 diastereomeric mixture of the tungsten-cobalt-alkyne complexes **5a** and **5b**, as shown in Eq. (4).



Ready vertex substitution is observed in the formation of $[\text{CoNi}(\mu\text{-PhC}_2\text{Ph})(\text{CO})_3\text{Cp}]$, which can be prepared by the reactions of $[\text{Ni}_2(\mu\text{-PhC}_2\text{Ph})\text{Cp}_2]$ with $[\text{Co}_2(\text{CO})_8]$, $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{CO})_6]$ with nickelocene, $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{CO})_6]$ with $[\text{Ni}_2(\mu\text{-PhC}_2\text{Ph})\text{Cp}_2]$, and diphenylacetylene with $[\text{Co}_3\text{Ni}(\text{CO})_9\text{Cp}]$ (Scheme 2).¹⁹ A related study reported the formation of $[\text{CoNi}(\mu\text{-PhC}_2\text{Ph})(\text{CO})_3\text{Cp}]$ from $[\text{Co}_2(\text{CO})_8]$, nickelocene, and diphenylacetylene.²⁰

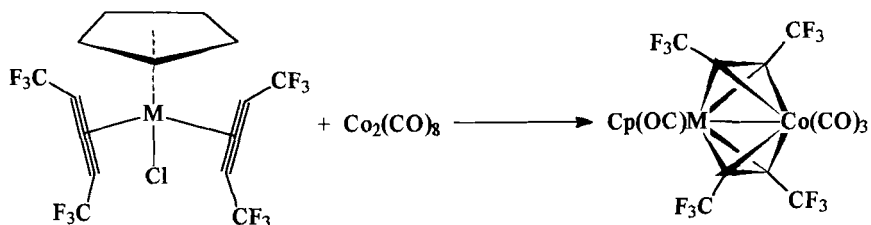
Reaction of transition-metal-propargyl complexes $\text{MCH}_2\text{C}\equiv\text{CR}$ with $[\text{Co}_2(\text{CO})_8]$ affords, as expected, $[\text{Co}_2(\mu\text{-MCH}_2\text{C}_2\text{R})(\text{CO})_6]$ ($\text{M} = \text{CpFe}(\text{CO})_2$, $\text{R} = \text{Ph}$, Me ; $\text{M} = \text{Mn}(\text{CO})_5$, $\text{R} = \text{Ph}$; $\text{M} = \text{CpW}(\text{CO})_3$, $\text{R} = \text{Ph}$, Me ; $\text{M} = \text{CpMo}(\text{CO})_3$, $\text{R} = \text{Ph}$) in which the propargyl complexes are coordinated via the triple bond to the hexacarbonyldicobalt fragment (Scheme 3). Treatment of the iron- or manganese-containing compounds ($\text{R} = \text{Ph}$) with acids leads to $\text{M}-\text{CH}_2$ bond cleavage and formation of $[\text{Co}_2(\mu\text{-PhC}_2\text{Me})(\text{CO})_6]$. In contrast, similar treatment of the molybdenum and tungsten complexes results in the formation of heterobinuclear complexes $[\text{MCo}(\mu\text{-RC}_2\text{Me})(\text{CO})_5\text{Cp}]$.²¹ Use of $\text{CF}_3\text{CO}_2\text{D}$ demonstrates that



SCHEME 2.

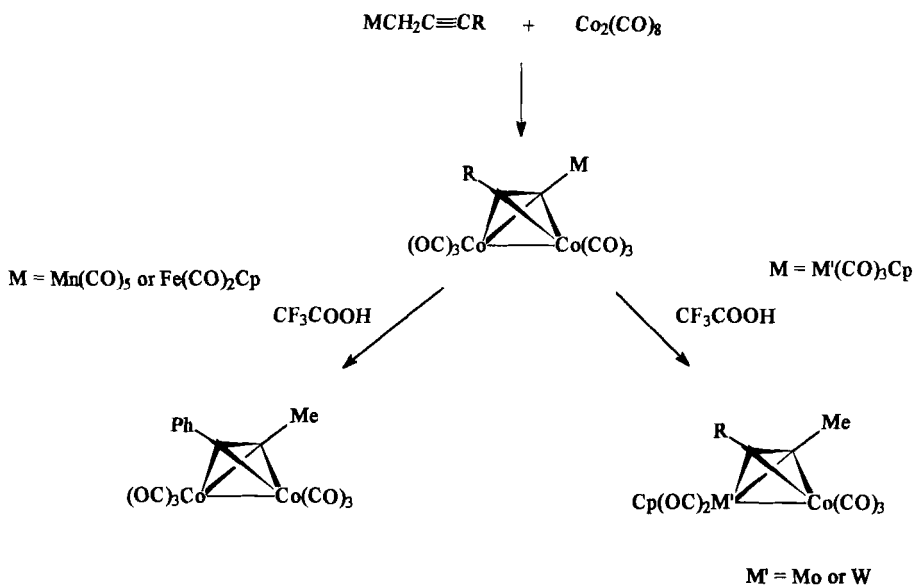
the additional hydrogen in the methyl group of the heterobinuclear complexes is derived from the acid. Protonation of a mixture of $[\text{Co}_2\{\mu\text{-Cp}(\text{OC})_3\text{WCH}_2\text{C}_2\text{Ph}\}(\text{CO})_6]$ and $[\text{Co}_2\{\mu\text{-Cp}'(\text{OC})_3\text{WCH}_2\text{C}_2(p\text{-tolyl})\}(\text{CO})_6]$ affords only $[\text{WCo}(\mu\text{-PhC}_2\text{Me})(\text{CO})_5\text{Cp}]$ and $[\text{WCo}\{\mu\text{-(}p\text{-tolyl)C}_2\text{Me}\}(\text{CO})_5\text{Cp}']$, illustrating that the reaction is intramolecular.²² In contrast, the related carbene compounds, $[\text{Co}_2(\mu\text{-}\eta^2\text{-PhC}_2\text{C}(\text{OEt})=\text{M}(\text{CO})_5)(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{W}$), rearrange in boiling hexane to give the triangular clusters $[\text{MCo}_2\{\mu_3\text{-}\eta^4\text{-CC}(\text{OEt})=\text{CPhC}(\text{O})\}(\mu\text{-CO})_2(\text{CO})_7]$ and the less stable isomers $[\text{MCo}_2\{\mu_3\text{-}\eta^4\text{-CCPh}=\text{C}(\text{OEt})\text{C}(\text{O})\}(\mu\text{-CO})_2(\text{CO})_7]$.²³

The heterobinuclear complexes $[\text{MCo}(\mu\text{-F}_3\text{CC}_2\text{CF}_3)_2(\text{CO})_3\text{Cp}]$ have been prepared by addition of octacarbonyldicobalt to the mononuclear alkyne complexes $[\text{M}(\text{F}_3\text{CC}_2\text{CF}_3)_2(\text{Cl})\text{Cp}]$ ($\text{M} = \text{Mo}$ or W),²⁴ demonstrating that cobalt-carbonyl fragments can coordinate to an alkyne already bound to another metal-ligand fragment; see Eq. (5).

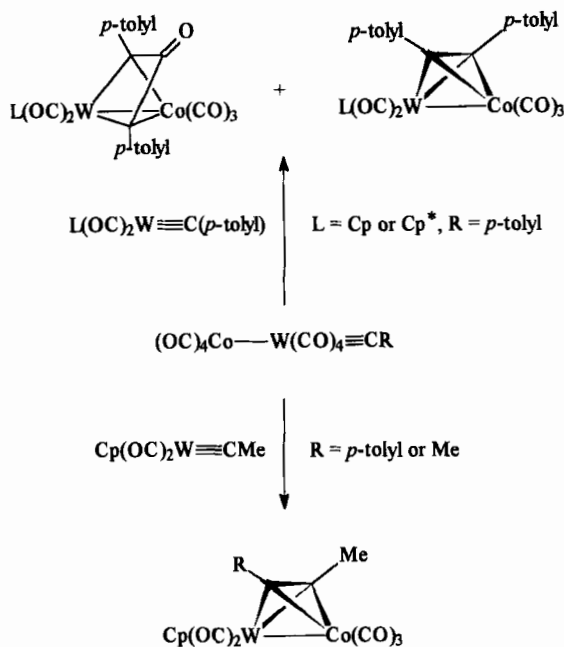


(5)

Tungsten-cobalt-alkyne complexes can be formed via alkylidyne coupling.²⁵ Reactions between the compounds $[\text{WCo}(\equiv\text{CR})(\text{CO})_8]$ and $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{L})]$ ($\text{R} = p\text{-tolyl}$, $\text{L} = \text{Cp}$ or Cp^*) afford chromatographically separable mixtures of $[\text{WCo}(\mu\text{-RC}_2\text{R})(\text{CO})_5(\text{L})]$ and $[\text{WCo}\{\mu\text{-C(R)C(O)C(R)}\}(\text{CO})_5(\text{L})]$ (Scheme 4). In contrast, the reaction between $[\text{WCo}(\equiv\text{CMe})(\text{CO})_8]$ and $[\text{W}(\equiv\text{CMe})(\text{CO})_2\text{Cp}]$ yields only the μ -alkyne complex $[\text{WCo}(\mu\text{-MeC}_2\text{Me})(\text{CO})_5\text{Cp}]$, whereas that between $[\text{WCo}(\equiv\text{C}(p\text{-tolyl}))(\text{CO})_8]$ and $[\text{W}(\equiv\text{CMe})(\text{CO})_2\text{Cp}]$ gives $[\text{WCo}\{\mu\text{-MeC}_2(p\text{-tolyl})\}(\text{CO})_5\text{Cp}]$.



SCHEME 3.



SCHEME 4.

The complexes $[\text{CoRh}(\mu\text{-RC}_2\text{R})(\text{CO})_6]$ ($\text{R} = \text{Ph}$ or C_6F_5) are formed by the reversible fragmentation of the tetranuclear clusters $[\text{Co}_2\text{Rh}_2(\mu_4\text{-}\eta^2\text{-RC}_2\text{R})(\text{CO})_{10}]$ (see Section IV).²⁶

B. Structures, Spectroscopy, and Bonding

The crystal structures of in excess of 70 hexacarbonylalkyne–dicobalt complexes have been determined by X-ray diffraction. In all cases the basic structural features are the same and can be illustrated by the structure of $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\text{CO})_6]$ shown in Fig. 1.²⁷ The molecule has pseudo C_{2v} symmetry in which the two cobalt atoms and the two acetylenic carbon atoms form a quasi-tetrahedral core. The carbon–carbon bond of the alkyne is in a perpendicular orientation relative to the cobalt–cobalt bond, as opposed to the parallel orientation which is also observed in dinuclear complexes with bridging alkyne ligands. The coordination around the cobalt atoms is distorted octahedral and the two tricarbonylcobalt moieties are eclipsed.

The average cobalt–cobalt bond distance found for hexacarbonylalkyne–dicobalt complexes in the Cambridge Crystallographic Data Base (January

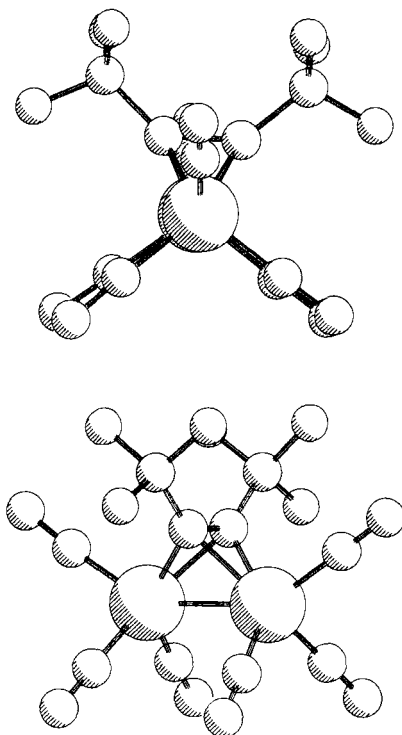


FIG. 1. Two views of the molecular structure of $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\text{CO})_6]$.

1996) is 2.467 \AA (limits 2.436 \AA^{28} to 2.498 \AA^{29}) and is short compared with that for octacarbonyldicobalt (ca. 2.52 \AA).³⁰ The alkyne bond is lengthened from ca. 1.20 \AA in free alkynes to, on average, 1.339 \AA (limits 1.284 \AA^{31} to 1.431 \AA^{32}). There appears to be little correlation between cobalt–cobalt and carbon–carbon distances, as illustrated in Fig. 2 (the correlation coefficient obtained from the best fit of the data is 0.200). In addition to the lengthening of the $\text{C}\equiv\text{C}$ bond upon coordination, the alkyne is distorted from linear. The average angle at the alkyne carbon atoms is 142.6° (limits 155.8^{33} to 118.5^{34}). These data are plotted in Fig. 3, and little correlation is observed between the carbon–carbon distance and the carbon–carbon–substituent angle (the correlation coefficient obtained from the best fit data is -0.308). The average cobalt–carbon distance is 1.969 \AA (limits 1.904 \AA^{34} to 2.085 \AA^{32}). There is some correlation between cobalt–carbon distance and the carbon–carbon–substituent angle, as illustrated in Fig. 4 (the correlation coefficient obtained from the best fit data is 0.538).²⁷

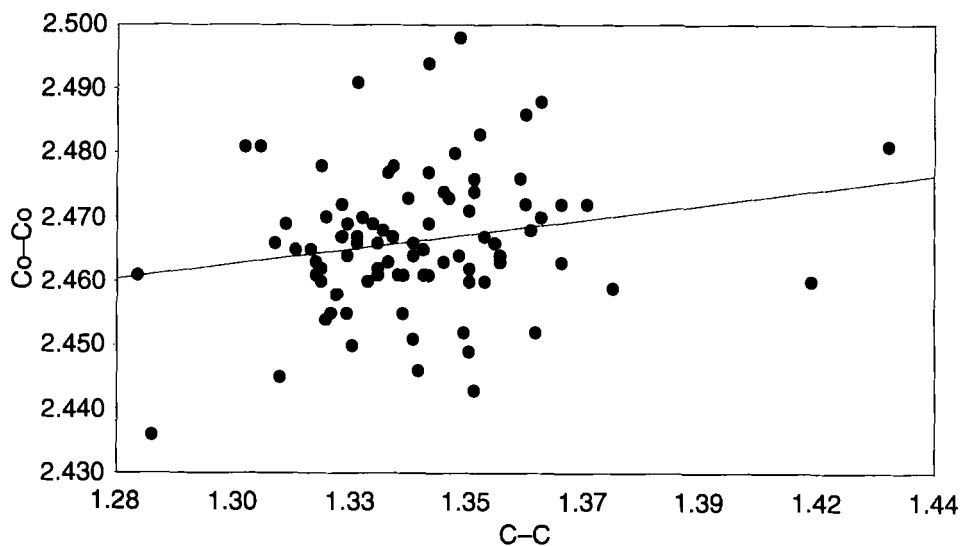


FIG. 2. Cobalt-cobalt bond length (Å) vs carbon-carbon bond distance (Å) for $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ complexes.

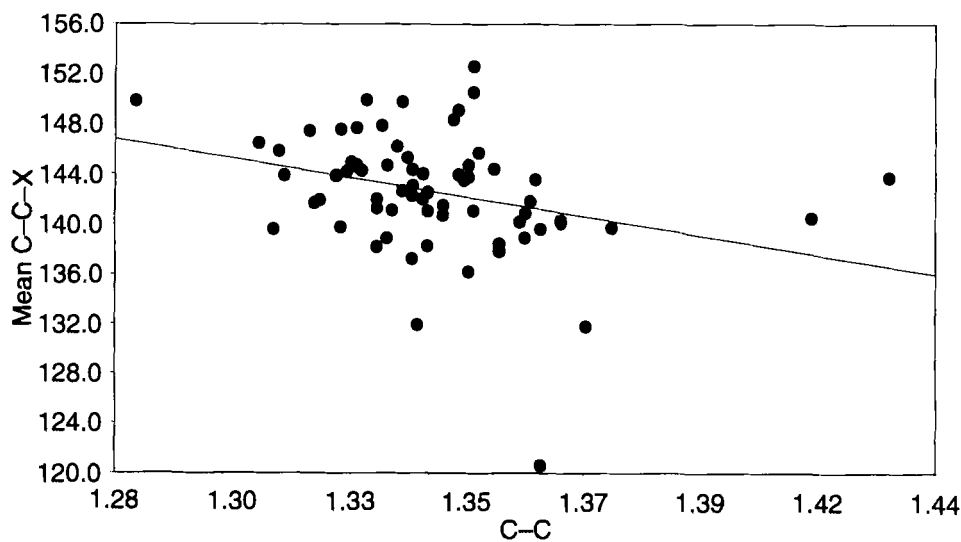


FIG. 3. Mean carbon-carbon-substituent angle ($^{\circ}$) vs carbon-carbon bond distance (Å) for $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ complexes.

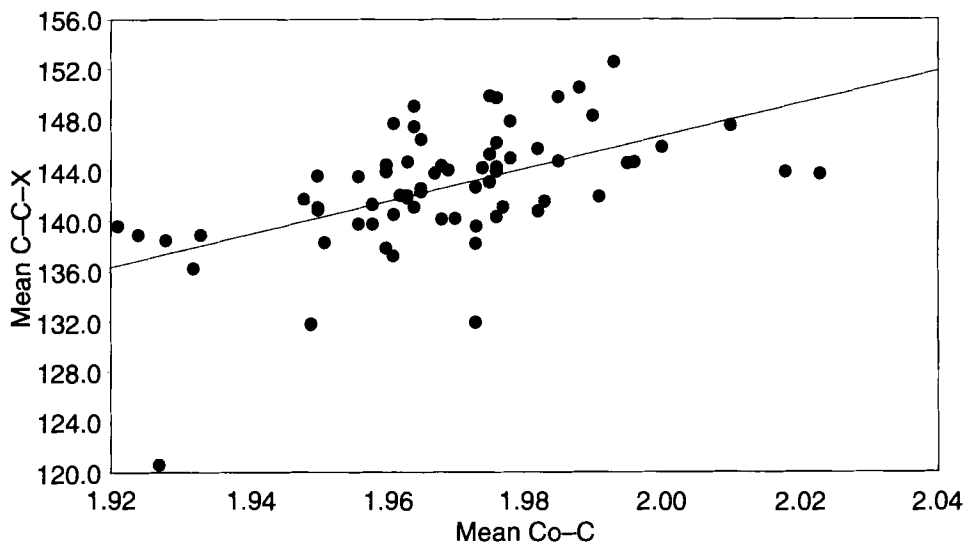


FIG. 4. Mean carbon-carbon-substituent angle ($^{\circ}$) vs mean cobalt-carbon bond distance (\AA) for $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ complexes.

Molecular orbital calculations for $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ complexes have been performed by Hoffmann at the extended Hückel level using $[\text{Co}_2(\mu\text{-HC}_2\text{H})(\text{CO})_6]$ as a model system.³⁵ The alkyne π orbitals of a_1 and b_2 symmetry, which are filled in the isolated ligand, are donor orbitals with respect to the metal-ligand interactions, whereas the originally empty π^* orbitals of a_2 and b_1 symmetry accept electrons from the metal d orbitals. The four alkyne orbitals interact with orbitals of the same symmetry from the "sawhorse"-shaped $\text{Co}_2(\text{CO})_6$ fragment to give four low-lying orbitals which, together with the a_1 σ orbital of the $\text{Co}_2(\text{CO})_6$ fragment, accommodate the six cobalt valence electrons and the four alkyne electrons. Figure 5 contains illustrations of these orbitals obtained using the CACAO program package.³⁶

Hoffmann found that the perpendicular orientation is preferred over the parallel orientation. The observation of alkyne rotation in the mixed-metal compound $[\text{CoNi}(\mu\text{-PhC}_2\text{CO}_2^i\text{Pr})(\text{CO})_3\text{Cp}]$ ³⁷ prompted a separate extended Hückel study, and **6** has been postulated as an intermediate in alkyne rotation, as shown in Eq. (6), and carbonyl and alkyne substitution reactions.³⁸

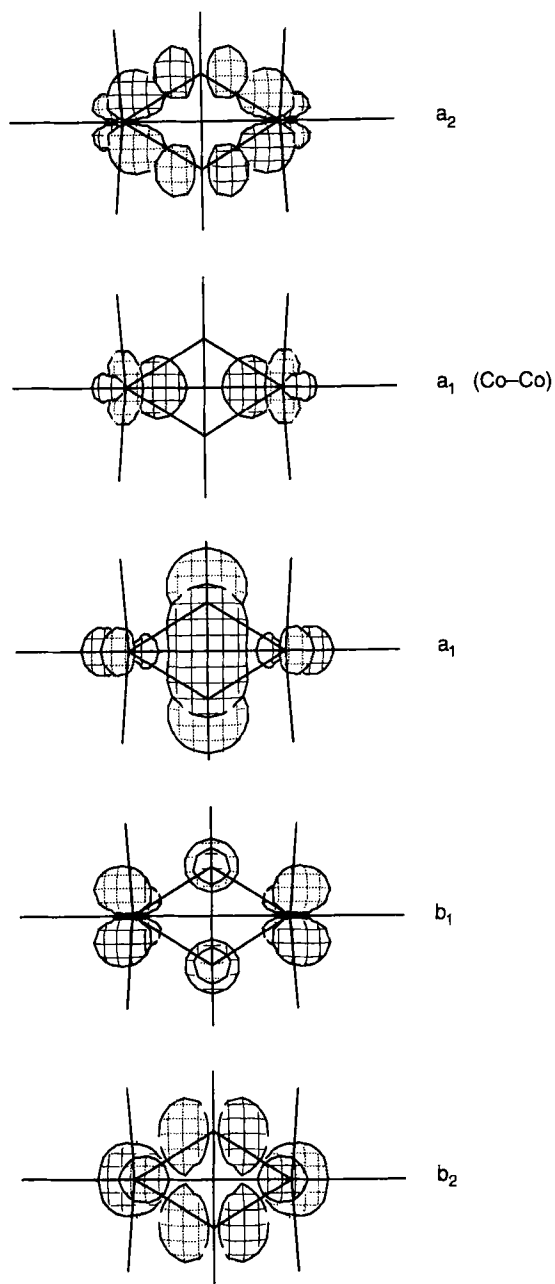
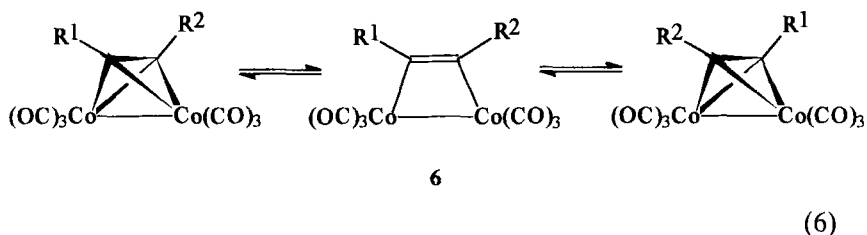
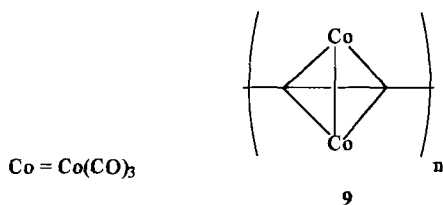
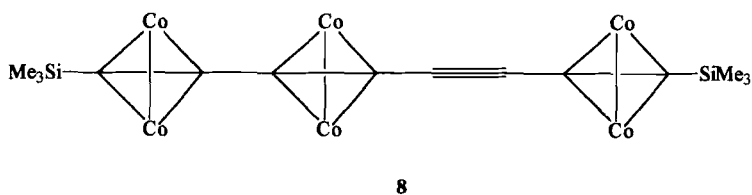
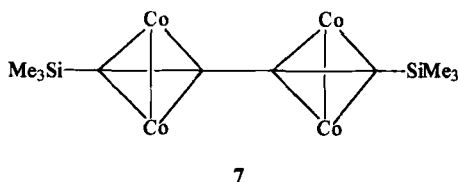


FIG. 5. Molecular orbitals of $[\text{Co}_2(\mu\text{-HC}_2\text{H})(\text{CO})_6]$ calculated using the CACAO program package viewed along the C_2 axis.



The electronic structure of oligomeric and polymeric systems based on hexacarbonylalkyne-dicobalt building blocks has also been studied by extended Hückel calculations.³⁹ Interest in such systems was generated by the synthesis of oligomers **7** and **8** and polymer **9** (see Formulae 7–9).⁴⁰ The calculations indicated that a significant amount of conjugation survives in the complexed carbon chains, but the polymers were predicted to be semiconductors with only moderate conductivity. The electronic structure of hexacarbonylalkyne-dicobalt complexes has also been investigated at the Fenske–Hall⁴¹ and *ab initio* LCAO-MO-SCF + CI levels.⁴²



FORMULAE 7–9.

The vibration spectroscopy of $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_{4-n}\text{L}_n]$ ($\text{L} = \text{PMe}_3$ or PPh_3 , $n = 0\text{--}2$) complexes has been studied in considerable detail.⁴³ The spectra display the following features:

- (a) Terminal alkynes show absorptions due to $\nu(\text{CH})$ at ca. 3100 cm^{-1} , a drop in frequency of ca. 200 cm^{-1} on complexation.
- (b) Up to six $\nu(\text{C}\equiv\text{O})$ vibrations between 2120 and 1900 cm^{-1} are observed, but in many cases only three strong bands are resolved.
- (c) The $\nu(\text{C}\equiv\text{C})$ bands lie in the region 1630 – 1490 cm^{-1} and are decreased by 710 – 560 cm^{-1} compared with the free alkynes, in accord with the decrease in carbon–carbon bond order.

Meyer has correlated the changes in $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}\equiv\text{O})$ frequency to evaluate the relative extent of σ - and π -bonding in these systems.⁴³ As expected $\sigma > \pi$ for alkyne complexes with electron-donating (or poorly attracting) substituents, $\sigma \approx \pi$ for alkyne complexes with one acceptor substituent, and $\sigma < \pi$ for alkyne complexes with two strongly electron-withdrawing substituents. Each of the two π -bonds of the alkyne releases approximately half of its electron population to form the σ -component of the alkyne–cobalt bonding, thus rendering each alkyne–cobalt bond analogous to the metal–alkene bond in complexes such as $[\text{Fe}(\eta^2\text{-alkene})(\text{CO})_4]$.

NMR spectroscopy is also a valuable probe for hexacarbonylalkyne–dicobalt complexes, and spectroscopic data for 34 representative $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ complexes have been tabulated.⁴⁴ Correlation of the ^{13}C NMR chemical shifts of the coordinated sp carbon atoms with those of the corresponding free alkynes reveals that the interaction between the substituent groups and the $\text{C}_2\text{Co}_2(\text{CO})_6$ moiety is very sensitive not only to the donor/acceptor character of the substituents but also to the orbital symmetry of the atoms directly attached to the sp carbon atoms. Upon coordination, $^1J(\text{CC})$ for $\text{HC}\equiv\text{CH}$ decreases from 171.5 to 55.9 Hz .⁴⁵

Spectroscopic data for mixed-metal complexes are consistent with data for structures in which the alkyne bridges the heteronuclear metal–metal bond in a $\mu\text{-}\eta^2, \eta^2$ fashion, as is found in the homodinuclear complexes $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$. This has been confirmed by X-ray crystallography in several cases.^{16,19,21,46–50}

C. Ligand Substitution

Reaction of $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ complexes with monodentate phosphines, phosphites, and arsines results in carbonyl ligand substitution.^{51,52} One or both axial carbonyl groups can be displaced under thermal conditions. This has been confirmed in a number of cases by X-ray crystallography, for example, $[\text{Co}_2(\mu\text{-HC}_2\text{H})(\text{CO})_4(\text{PMe}_3)_2]$ (Fig. 6).⁵³ The structure inherited from the parent compound is not greatly affected by substitution. The molecule still possesses C_{2v} symmetry and the cobalt–cobalt bond

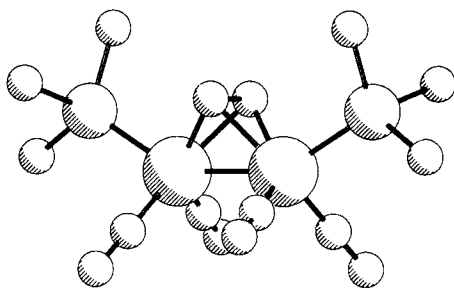
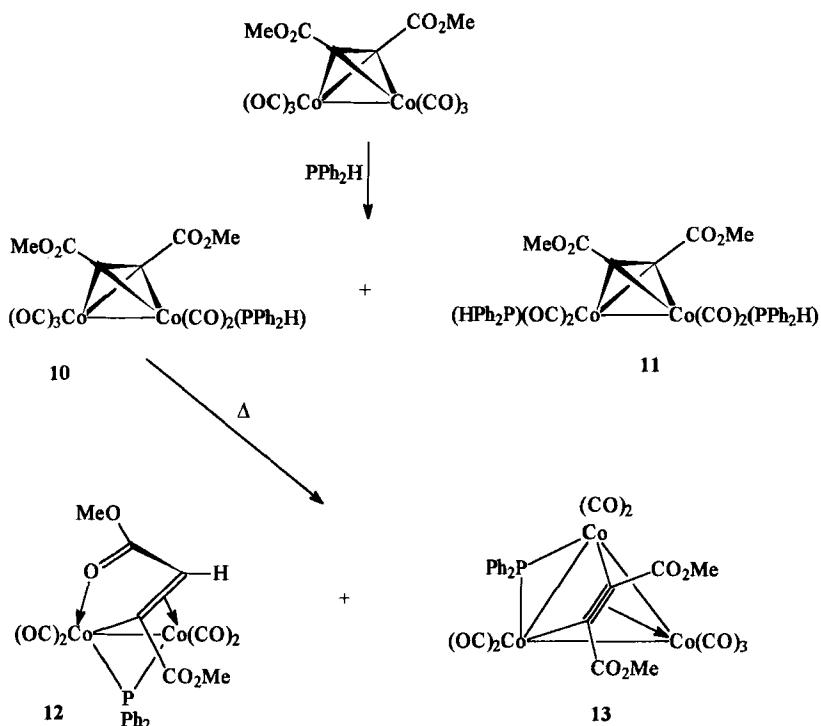


FIG. 6. The molecular structure of $[\text{Co}_2(\mu\text{-HC}_2\text{H})(\text{CO})_4(\text{PMe}_3)_2]$.

length is unchanged. The cobalt–carbonyl distances (average 1.782 Å) are significantly shortened (average for $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ ca. 1.804 Å) because of the poorer π -acceptor properties of phosphine ligands compared with carbonyls.

Up to four carbonyl ligands can be displaced when $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{CO})_6]$ is treated with $\text{P}(\text{OMe})_3$ in refluxing toluene to afford $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{CO})_{6-n}(\text{P}(\text{OMe})_3)_n]$ ($n = 1\text{--}4$).⁵¹ The last two substitutions can be reversed by treatment with carbon monoxide to afford $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{CO})_4(\text{P}(\text{OMe})_3)_2]$. Phosphine and phosphite substituted products can also be prepared electrocatalytically.^{54,55} Substitution with secondary phosphines has also been studied and is of interest because P–H bond cleavage in dinuclear complexes containing secondary phosphines can lead to hydrogen transfer and hence modification of the coordinated organic ligand. Reaction of $[\text{Co}_2(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_6]$ with 1 eq of PPh_2H in toluene at 323 K affords the simple substitution products $[\text{Co}_2(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_5(\text{PPh}_2\text{H})]$ (**10**) and $[\text{Co}_2(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{CO})_4(\text{PPh}_2\text{H})_2]$ (**11**) in 70 and 10% yields, respectively.⁵⁶ Thermolysis of the monosubstituted complex **10** at 333 K in toluene for 40 h does indeed cause P–H bond cleavage and formation of the phosphido-, vinyl-bridged complex $[\text{Co}_2\{\mu\text{-C}(\text{CO}_2\text{Me})=\text{CHCO}_2\text{Me}\}(\mu\text{-PPh}_2)(\text{CO})_4]$ (**12**) as the major product. The trimeric complex $[\text{Co}_3\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\mu\text{-PPh}_2)(\text{CO})_7]$ (**13**) is also isolated from the reaction (Scheme 5) as a minor product.

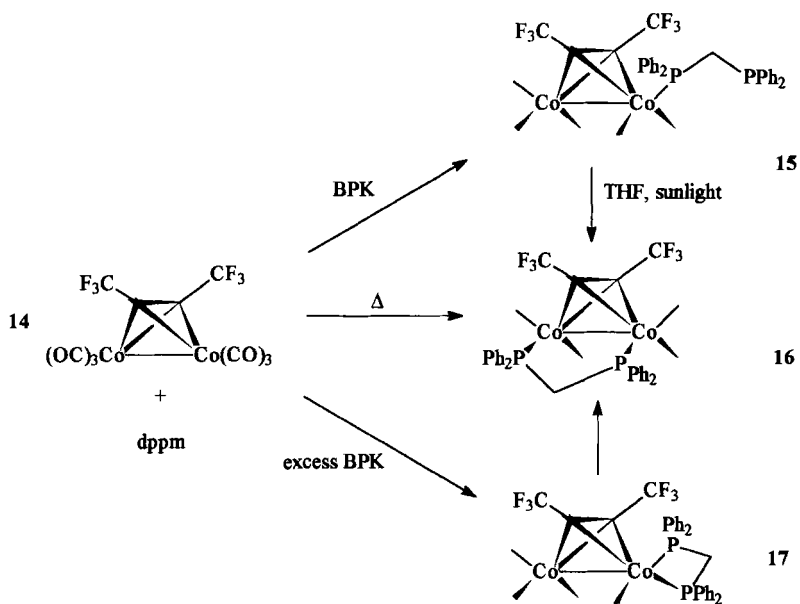
Substitution reactions employing bidentate phosphine ligands afford both bridged and chelated products of the type $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_{6-2n}(\text{L-L})_n]$. The exact nature of the product depends on the phosphine and the reaction conditions. Thermal ligand substitution with *dp*pm or *dp*pe affords the phosphine-bridged isomers, whereas electron transfer catalysis gives the chelated or bridged complexes.⁵⁷ In particular, a detailed study has been reported of the substitution reactions of $[\text{Co}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{CO})_6]$ with *dp*pm, *dp*pe, or *ttas* [bis(*o*-(dimethylarsino)phenyl)methylarsine] initiated



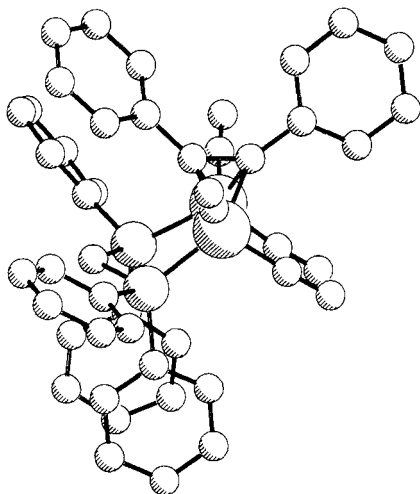
SCHEME 5.

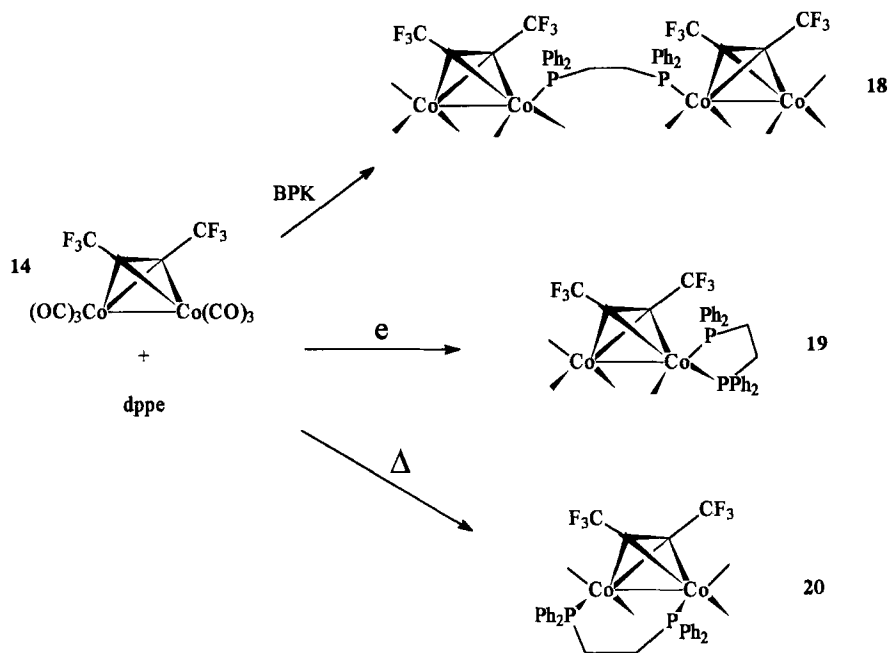
by catalytic (electrochemical or chemical) or thermal methods.^{58,59} The complex $[\text{Co}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{CO})_6]$ was chosen because previous studies had shown that its radical anion is thermodynamically and kinetically stable. Products and yields were dependent on method of initiation, solvent, temperature, and ligand.

Addition of a catalytic amount of BPK to a **14**/dppm/THF solution at 288 K affords a quantitative yield of **15**, in which the dppm is monodentate, within 1 min (Scheme 6). The thermal reaction of **14** with dppm in hexane affords the dppm-bridged complex, **16**. The substitution of equatorial carbonyls to form $\mu\text{-}\eta^2\text{-dppm}$ products has been confirmed in a number of cases by X-ray crystallography, for example, $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\mu\text{-dppm})(\text{CO})_4]$ (Fig. 7).⁶⁰ Solution dynamics studies of $[\text{Co}_2(\mu\text{-alkyne})(\mu\text{-dppm})(\text{CO})_4]$ complexes show that an effective mirror plane that contains the cobalt-cobalt bond and the two phosphorus atoms is generated on the NMR time scale.⁶¹ This can be interpreted as a rocking motion of the alkyne about the cobalt-cobalt bond. Complex **16** is also produced



SCHEME 6.

FIG. 7. The molecular structure of $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\mu\text{-dppm})(\text{CO})_4]$.



SCHEME 7.

together with **17** when the BPK-initiated reactions are left for several minutes before workup or when an excess of BPK is used. Ring closure of **15** to **16** is rapid in THF in sunlight ($t_{1/2} \approx 5$ min at 298 K), but negligible in hexane or CH_2Cl_2 . Even at 273 K **17** rapidly converts to **16** in all solvents.

The BPK-initiated reaction of **14** with dppe in THF at 293 K gives near quantitative yields of the linked complex **18** (Scheme 7). The "thermal" reaction of **14** with dppe is also fast at 293 K and affords **18**, **19**, and trace amounts of **20**. Better yields of **19** are obtained in refluxing hexane, and a selective conversion to **19** is achieved by a cathode-induced reaction at -0.65 V in CH_2Cl_2 . The structure of **19** was determined by X-ray crystallography and confirms the chelating nature of the dppe coordination (Fig. 8).

The initial product of the BPK-catalyzed reaction of **14** with ttas is the labile derivative **22**, which can be converted into the thermally stable, fully ligated product **23** (Scheme 8). Compound **23** is the only product obtained from a thermal reaction in refluxing toluene, but at room temperature in THF traces of **21** which convert to **23**, presumably via **22**, are also obtained. The η^2 and η^3 coordination of ttas in **22** and **23** has been confirmed by X-ray crystallography (Fig. 9).

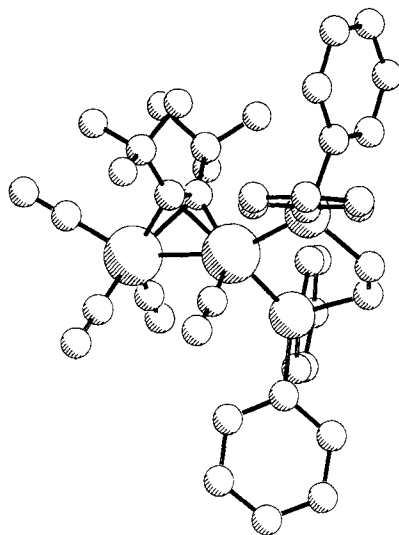
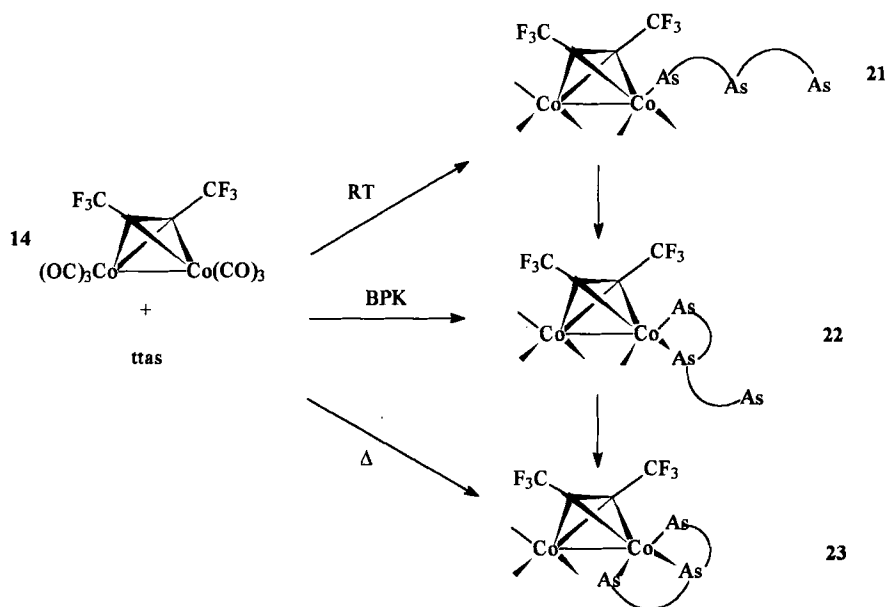


FIG. 8. The molecular structure of $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\eta^2\text{-dppe})(\text{CO})_4]$.



SCHEME 8.

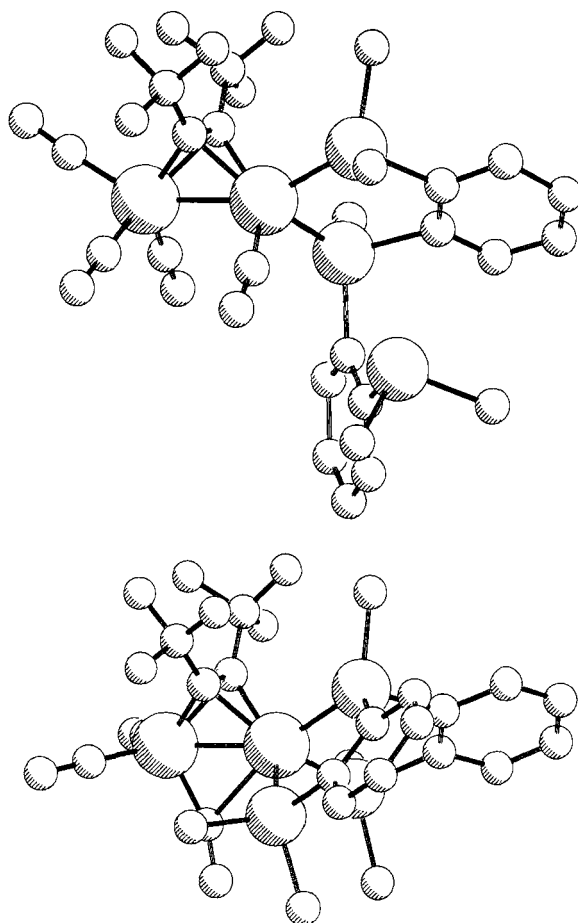


FIG. 9. The molecular structures of $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\eta^2\text{-ttas})(\text{CO})_4]$ (top) and $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\eta^3\text{-ttas})(\text{CO})_3]$ (bottom).

Substitution of hexacarbonylalkyne-dicobalt complexes can also be activated at room temperature using oxidative decarbonylation with Me_3NO . A detailed study has been conducted with the unsaturated diphosphine ligand bma [2,3-bis(diphenylphosphino)maleic anhydride].⁶² Reaction of $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{CO})_6]$ with bma and Me_3NO at room temperature affords the chelating isomer $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\eta^2\text{-bma})(\text{CO})_4]$, whereas the thermal reaction affords a mixture of chelating and bridging isomers. Isomerization studies suggest consecutive reaction pathways in which the initially chelating isomer is an intermediate in the formation of the bridging isomer. Similar studies between $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{CO})_6]$ and $(Z)\text{-Ph}_2\text{CH=CHPPh}_2$ af-

forded only the chelating isomer, indicating that this diphosphine remains associated with the original cobalt center.

Connelly and Orpen have used the complexes $[\text{Co}_2(\mu\text{-RC}_2\text{R})(\mu\text{-dppm})_2(\text{CO})_2]$ ($\text{R} = \text{Me}, \text{Ph}, \text{or } \text{CO}_2\text{Me}$) to test the molecular orbital description of $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ outlined in Section II,B.^{63a} The X-ray crystal structures of $[\text{Co}_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2(\text{CO})_2]$ (see Fig. 10) and $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\mu\text{-dppm})_2(\text{CO})_2]$ show the alkyne to be orthogonal to the cobalt-cobalt bond. Oxidation affords the monocations $[\text{Co}_2(\mu\text{-RC}_2\text{R})(\mu\text{-dppm})_2(\text{CO})_2]^+$, and the crystal structure of $[\text{Co}_2(\mu\text{-MeC}_2\text{Me})$

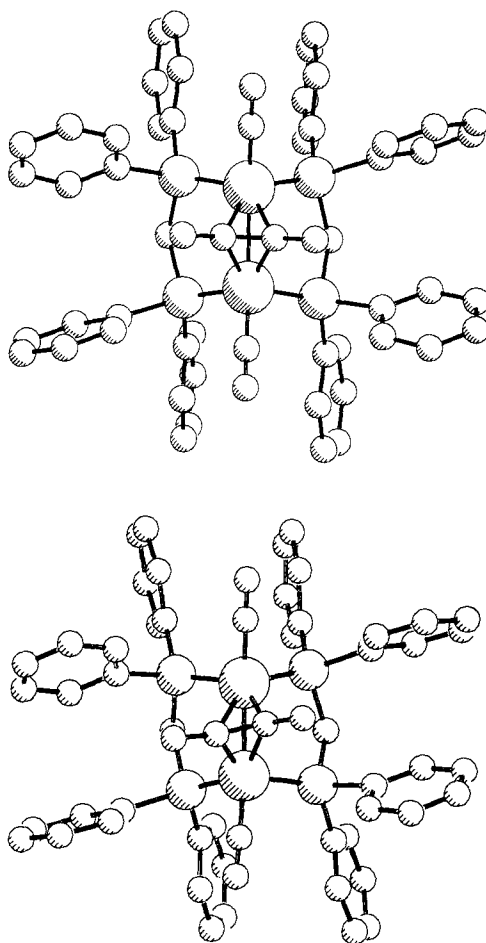


FIG. 10. The molecular structures of $[\text{Co}_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2(\text{CO})_2]$ (top) and $[\text{Co}_2(\mu\text{-MeC}_2\text{Me})(\mu\text{-dppm})_2(\text{CO})_2]^+$ (bottom).

$(\mu\text{-dppm})_2(\text{CO})_2[\text{PF}_6]$ has been determined (see Fig. 10). The effects of the one-electron oxidation are dramatic. The cobalt–cobalt bond length is reduced by almost 0.1 Å, and the alkyne carbon–carbon bond in the cation is twisted by 12.0° relative to the ideal transverse orientation. Thorn and Hoffmann^{63b} suggested that alkyne rotation of ca. 20° would be induced in 32e species as a consequence of a second-order Jahn–Teller effect arising from a low-lying vacant orbital of a_2 symmetry interacting with the a_2 HOMO. The observed value of 12° for a one-electron oxidation (i.e. for the 33e species) is in agreement with these predictions. Also, the singly occupied molecular orbital of the cation would be expected (assuming a MO pattern similar to that of the hexacarbonyl derivatives) to be cobalt–cobalt π -antibonding in character (see Fig. 5) and is in accord with the shortening of the cobalt–cobalt distance.

Substitution reactions to afford chiral complexes have been of particular interest because they offer the possibility of performing asymmetric reactions and catalysis. Any monosubstituted system with an asymmetric alkyne, $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{R}^2)(\text{CO})_5\text{L}]$, is inherently chiral. If the alkyne has a chiral center, then diastereomers will exist. The basic substitution reactions are described in this section, and their application to organic synthesis is amplified in Section VI. Reaction of racemic propargylic alcohol complexes $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{CH}(\text{OH})\text{R}^2)(\text{CO})_6]$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$, Ph, *t*-Bu; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, *i*-Pr) with 0.8 eq PPh_3 affords the monosubstituted derivatives, $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{CH}(\text{OH})\text{R}^2)(\text{CO})_5(\text{PPh}_3)]$, in excellent yield.⁶⁴ When $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$, Ph, or $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, analysis of the crude products indicates a mixture of two diastereomers. The remaining two derivatives were formed as a single isomer, indicating diastereomeric excesses greater than 95%. Significantly, the diastereomeric mixtures can be separated chromatographically and exhibit considerable configurational stability. The minor isomers were found to isomerize and disproportionate very slowly in solution at 20°C ($t_{1/2} = \text{ca. } 50\text{--}200 \text{ h}$) to produce mixtures containing the major isomer, the disubstituted complex, and the hexacarbonyl complexes. This suggests that phosphine dissociation and readdition may account for the isomerization. Crossover experiments support this hypothesis, but intramolecular isomerization such as an alkyne twist [Eq. (6)] or other cluster skeletal rearrangements are hard to exclude. Related diastereoselectivity has been observed in reactions of $[\text{Co}_2(\mu\text{-HC}_2\text{Ph})(\text{CO})_6]$ with the optically active phosphine “glyphos,” which result in two diastereomers, differing only in the chirality of the Co_2C_2 units, which can be separated by preparative liquid chromatography.⁶⁵ Epimerization occurs at 60°C with $t_{1/2} = 170 \text{ min}$, which is slow enough to allow stereoselective Pauson–Khand reactions with norbornene (see Section VI). However, with less reactive alkenes, which necessitate longer reaction times, poorer results are obtained because of the

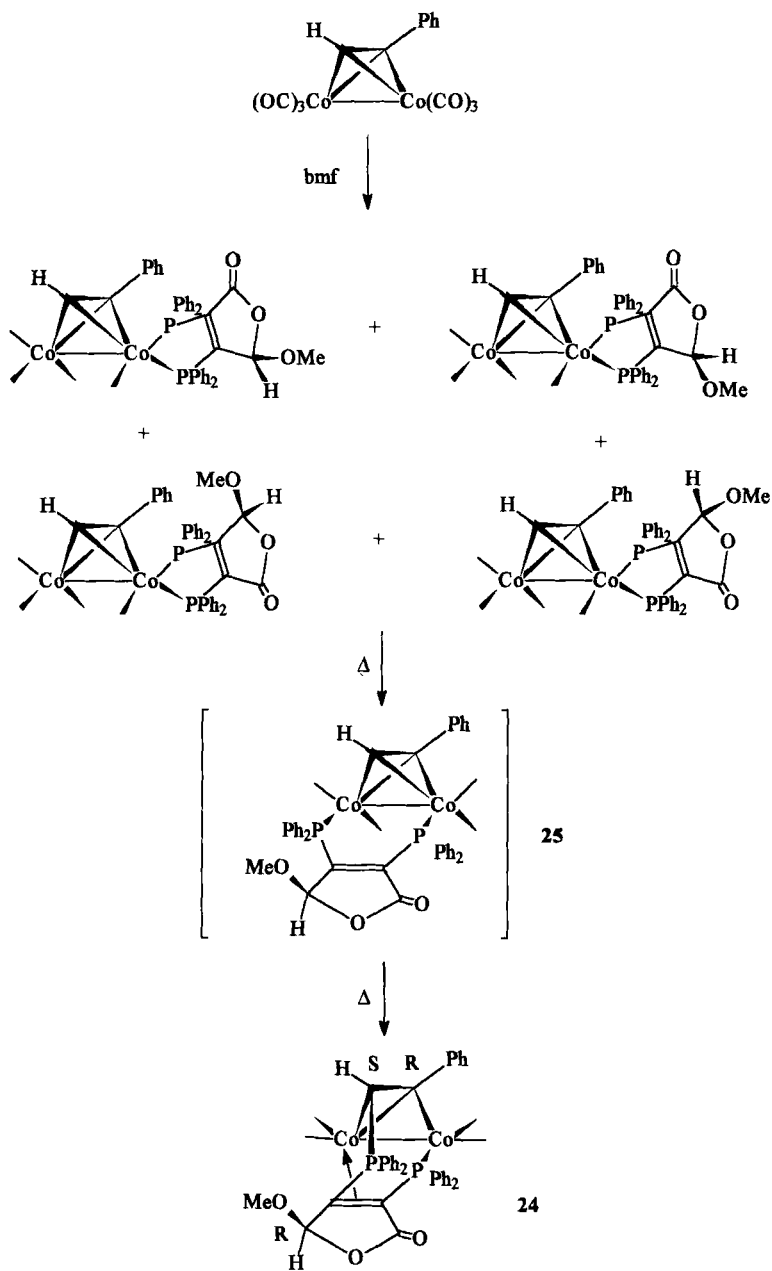
easy loss of phosphine and hence interconversion of the two diastereomeric forms of starting material. D'Agostino *et al.*¹⁸ have shown that bornyl and menthyl complexes such as **5** react with phosphines with poor enantioselectivity. Also discouraging is the reaction of homochiral hexacarbonyl (cholesteryl propargyl ether) dicobalt with P(OMe)_3 , which proceeds without stereoselectivity.⁶⁶ The diastereomeric product mixture suffers metal-carbon rather than oxygen-carbon cleavage on treatment with acid, precluding the use of either diastereomer in the Nicholas reaction (see Section II,D).⁶⁶ Although considerable progress has been made, there is still much work to be done in the development of chiral dicobalt-alkyne complexes.

The Me_3NO -activated carbonyl substitution of $[\text{Co}_2(\mu\text{-PhC}_2\text{H})(\text{CO})_6]$ with the diphosphine ligand bmf [3,4-bis(diphenylphosphino)-5-methoxy-2(5*H*)-furanone] affords the chelating diphosphine complex $[\text{Co}_2(\mu\text{-PhC}_2\text{H})(\text{CO})_4(\text{bmf})]$ with four diastereomers.⁶⁷ Thermolysis of the mixture proceeds smoothly to afford **24** with 100% diastereoselectivity and PPh_2 regioselectivity, possibly via the bridging isomer **25** (Scheme 9).

Thermal reaction of $[\text{CpMo}(\text{CO})_2(\mu\text{-alkyne})\text{Co}(\text{CO})_3]$ with phosphine ligands affords monosubstituted derivatives, $[\text{CpMo}(\text{CO})_2(\mu\text{-alkyne})\text{Co}(\text{CO})_2\text{L}]$, in which the phosphine is coordinated to the cobalt center.^{14,16,68}

Carbonyl substitution with ligands other than phosphines, phosphites, or arsines has received comparatively little attention. Reaction of $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\text{CO})_6]$ with CH_3CN can be performed thermally, electrochemically, or with benzophenoneketyl to afford $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\text{CO})_5(\text{NCCH}_3)]$. In contrast to monophosphines, the CH_3CN ligand occupies an equatorial site (Fig. 11).⁵⁵ A similar structure has been postulated for $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\text{CO})_5(\text{NCC}(\text{CH}_3)_2\text{N}_2\text{C}(\text{CH}_3)_2\text{CN})]$ obtained from the reaction of $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\text{CO})_6]$ with 2,2'-azobis(2-methylpropionitrile).¹⁶ The PdO-catalyzed reaction of $[\text{CpMo}(\text{CO})_2(\mu\text{-RO}_2\text{CC}_2\text{CO}_2\text{R})\text{Co}(\text{CO})_3]$ ($\text{R} = \text{Me}$ or Et) with the isocyanides $\text{R}'\text{NC}$ ($\text{R}' = t\text{-Bu}$, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) results in substitution at the cobalt center to afford $[\text{CpMo}(\text{CO})_2(\mu\text{-RO}_2\text{CC}_2\text{CO}_2\text{R})\text{Co}(\text{CO})_{3-x}(\text{CNR}')_x]$ ($x = 1, 2$).¹⁴

Reaction of Ph_2PSPH with $[\text{Co}_2(\mu\text{-HC}_2\text{H})(\text{CO})_6]$ leads to P-S bond cleavage and the formation of metallocyclic complexes with either Ph_2P or PhS fragments incorporated into the bridging organic ligand.⁶⁹ In contrast, treatment of $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{R}^2)(\text{CO})_6]$ ($\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$ or $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CO}_2\text{Me}$) with $\text{Ph}_2\text{PCH}_2\text{SR}$ ($\text{R} = \text{Me}$ or Ph) affords the monosubstituted complexes $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{R}^2)(\eta^1\text{-PPh}_2\text{CH}_2\text{SR})(\text{CO})_5]$, in which the incoming ligand is bound through only the phosphine center in, presumably, an axial position.⁷⁰ When the complexes $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{R}^2)(\eta^1\text{-PPh}_2\text{CH}_2\text{SR})(\text{CO})_5]$ are heated, loss of CO leads to the bridged species $[\text{Co}_2(\mu\text{-R}^1\text{C}_2\text{R}^2)(\mu\text{-PPh}_2\text{CH}_2\text{SR})(\text{CO})_4]$ with both the phosphine and thio-



SCHEME 9.

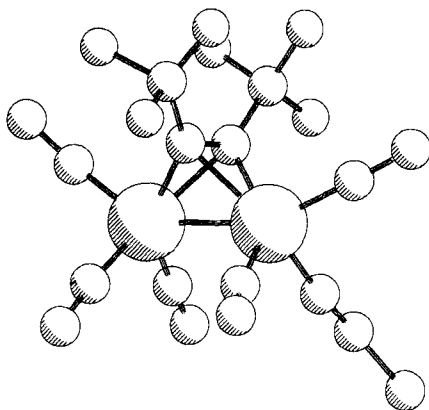


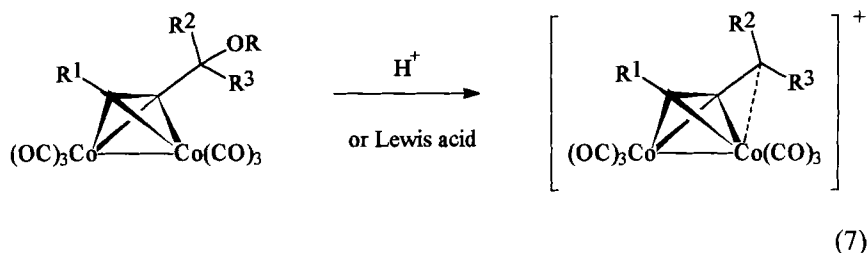
FIG. 11. The molecular structure of $[\text{Co}_2(\mu\text{-F}_3\text{CC}_2\text{CF}_3)(\text{NCMe})(\text{CO})_5]$.

ether groups bound in equatorial positions. This transformation is readily reversed by treatment with CO, indicating that the $\text{Co}-\text{S}$ bond is relatively weak. Thioether coordinated complexes have been postulated as intermediates in Pauson-Khand reactions of sulfur-substituted substrates (see Section VI).⁷¹

D. Cationic Species

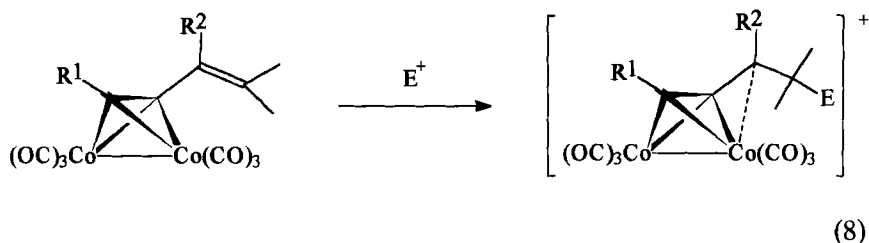
1. Synthesis of Monocationic Species

The chemistry and synthetic utility of cobalt complexed propargyl cations have been demonstrated by Nicholas in an impressive series of papers, and the area was reviewed in 1987.⁷² More recently, reviews of cluster-stabilized cations⁷³ and propargylium complexes⁷⁴ have appeared. Two general routes for the synthesis of dicobalt-propargylium complexes have been developed. The most commonly used method is the treatment of an alkynic ether or alkynic alcohol-hexacarbonyldicobalt complex with a Lewis or Brønsted acid [Eq. (7)].

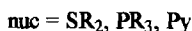
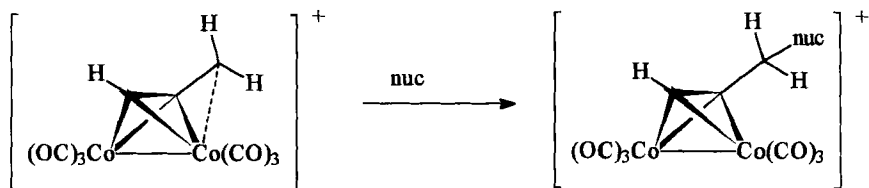


The reaction is typically performed in diethyl ether, and the dication is precipitated as a red-brown solid or oil. Mixed-metal molybdenum-cobalt and tungsten-cobalt systems have also been obtained by this technique.^{75,76}

Enyne complexes can also act as precursors to dicobalt-propargylium complexes via their reactions with electrophiles, as shown in Eq. (8).^{77,78}



In order to increase the stability of the reactive carbenium species and modify their reactivity, the effects of attachment of sulfide, pyridine, and phosphine groups on the α carbon have been studied (see Section II,D,3). Treatment of $[Co_2(\mu, \eta^2, \eta^3-HC_2CH_2)(CO)_6]^+$ with the nucleophiles ($nuc = SR_2$, PR_3 , and Py) affords the cationic complexes $[Co_2(\mu, \eta^2, \eta^2-HC_2CH_2nuc)(CO)_6]^+$ in high yields, as shown in Eq. (9).⁷⁹



(9)

2. Characterization of Monocationic Species

The $[Co_2(\mu, \eta^2, \eta^3-RC_2CR_2)(CO)_6]^+$ species are more reactive and considerably less stable than the analogous dimolybdenum, ditungsten, or molybdenum/tungsten-cobalt species. The greater reactivity and ready preparation of the dicobalt systems have led to their extensive use in derivatization of the coordinated alkyne, whereas the greater stability of Group 6-containing compounds has facilitated their more detailed structural and spectroscopic characterization. For example, a number of X-ray crystal structures of dimolybdenum monocations have been reported,⁸⁰⁻⁸⁷ all of which

confirm that the “cationic” carbon center is stabilized by interaction with an electron-rich molybdenum center, but as yet there has been no reported crystal structure determination of a $[\text{Co}_2(\mu, \eta^2, \eta^3\text{-RC}_2\text{CR}_2)(\text{CO})_6]^+$ complex. X-ray crystal structures of the mixed-metal complexes $[\text{MoCo}(\mu, \eta^2, \eta^3\text{-2-propynylbornyl})(\text{CO})_5\text{Cp}][\text{BF}_4]$ (Fig. 12) and $[\text{MoCo}(\mu, \eta^2, \eta^3\text{-HC}_2\text{CHMe})(\text{CO})_5\text{Cp}][\text{BF}_4]$ have been obtained and they show that the carbenium centers are bent toward the molybdenum atoms, confirming the greater ability of a Group 6 metal center to stabilize the positive charge.^{88,89} This preference is also confirmed by spectroscopic observations and EHMO calculations.⁸⁸ The relative ability of metal–ligand fragments to stabilize cations has been shown to be $\text{Mo}_2\text{C}_2(\text{CO})_4\text{Cp}_2 > \text{Fc} > \text{Co}_2\text{C}_2(\text{CO})_6$.⁹⁰

The difficulty of obtaining single crystals of a $[\text{Co}_2(\mu, \eta^2, \eta^3\text{-RC}_2\text{CR}_2)(\text{CO})_6]^+$ species has limited their characterization to spectroscopic methods, but nevertheless considerable insight into their structures has been gained. IR spectroscopic data give evidence for charge delocalization onto the $\text{Co}_2(\text{CO})_6$ moiety. The carbonyl stretching frequencies for the cations are increased by $40\text{--}60\text{ cm}^{-1}$ relative to the neutral complexes, indicating a diminution of cobalt–carbonyl back donation due to an increase of positive charge on the cobalt centers.⁹¹ The fluxional nature of the $[\text{Co}_2(\mu, \eta^2, \eta^3\text{-RC}_2\text{CR}_2)(\text{CO})_6]^+$ complexes was established by Nicholas.⁹² The cation $[\text{Co}_2(\mu, \eta^2, \eta^3\text{-RC}_2\text{CMe}_2)(\text{CO})_6]^+$ exhibits one methyl signal in the ^{13}C NMR spectrum at 0°C which separates into two sharp signals below -40°C . This is consistent with a structure in which the positive charge is not merely sited on an upright α -carbon but is delocalized via a direct bonding interaction with a cobalt center. Further elegant NMR studies

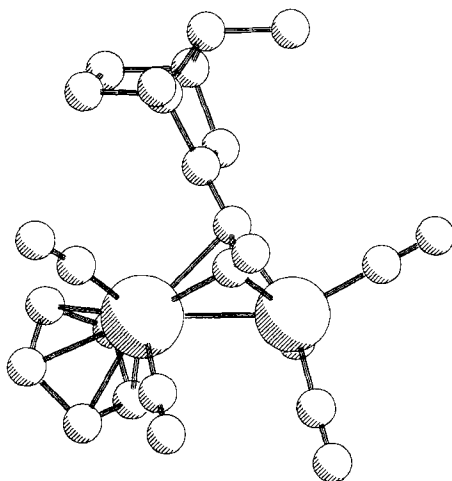
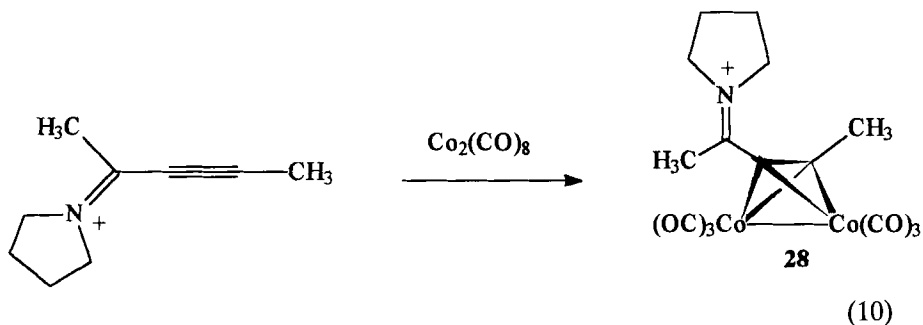


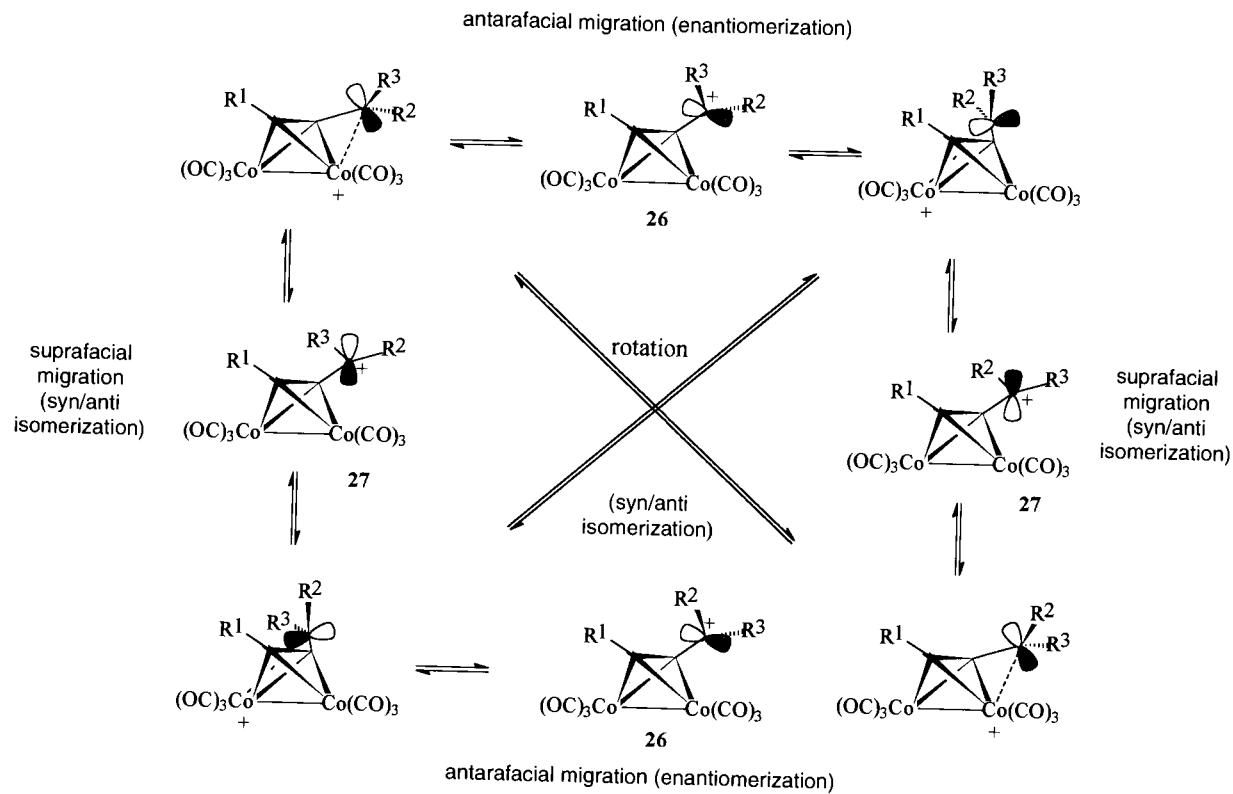
FIG. 12. The molecular structure of $[\text{MoCo}(\mu, \eta^2, \eta^3\text{-2-propynylbornyl})(\text{CO})_5\text{Cp}]^+$.

have been performed by Schrieber, who established the existence of two fluxional processes, as depicted in Scheme 10.⁹³ The two processes are (i) a low-energy (ca. 10 kcal mol⁻¹) antarafacial migration of the carbocation from one Co(CO)₃ to the other, which results in enantiomerization, and (ii) a higher energy (ca. 13 kcal mol⁻¹) process involving 180° rotation of the carbocation or suprafacial migration, which results in diastereomerization. The transition state for the enantiomerization may resemble the upright structure **26**, which is capable of maintaining partial delocalization of the carbon *p*-orbital into the hybrid *d*-orbitals on the neighboring cobalt atoms. The increased energetic requirements for achieving diastereomerization may be associated with the requirement for achieving the rotated upright structure **27**, which localizes charge on the α -carbon. This latter proposal is in accord with the observation that the activation energy barrier for this second fluxional process is lower for tertiary than for secondary cations because the more stable tertiary carbocation has less need for anchimeric assistance from a cobalt center. In the heterobimetallic molybdenum-cobalt stabilized propargylium ions, only one fluxional mechanism is involved in isomerization. This mechanism appears to be a 180° rotation of the carbocation at the molybdenum center.⁹⁴

The structure of the cationic complex [Co₂(μ , η^2 , η^2 -HC₂CH₂PEt₃)(CO)₆]⁺ has been established by an X-ray diffraction study (Fig. 13).⁷⁹ The main difference between this type of cationic derivative and the parent propargylium complexes is the absence of any anchimeric assistance from the cobalt to the carbocation center. The cobalt-carbon interaction is replaced by a direct interaction with the heteroatom of the nucleophile. This is reflected in the infrared spectra of the [Co₂(μ , η^2 , η^2 -HC₂CH₂nuc)(CO)₆]⁺ species. The values of the carbonyl stretching bands lie in between those of [Co₂(μ , η^2 , η^2 -HC₂CH₂OH)(CO)₆] and [Co₂(μ , η^2 , η^3 -HC₂CH₂)(CO)₆]⁺.

A similar effect has been observed in a study of charge dispersal in iminium-substituted alkynes. In the structure of **28** the iminium character of the alkyne is preserved, and significant charge delocalization onto the dicobalt unit does not occur; see Eq. (10).⁹⁵





SCHEME 10.

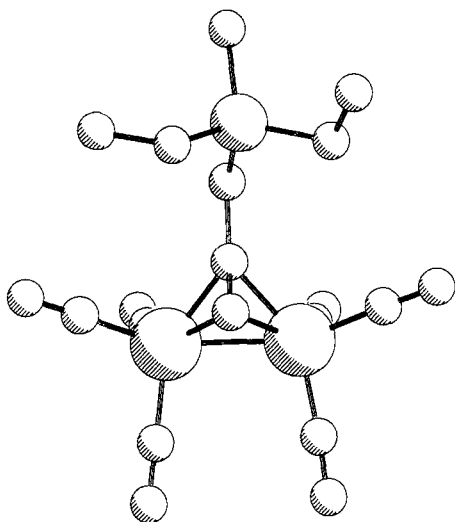


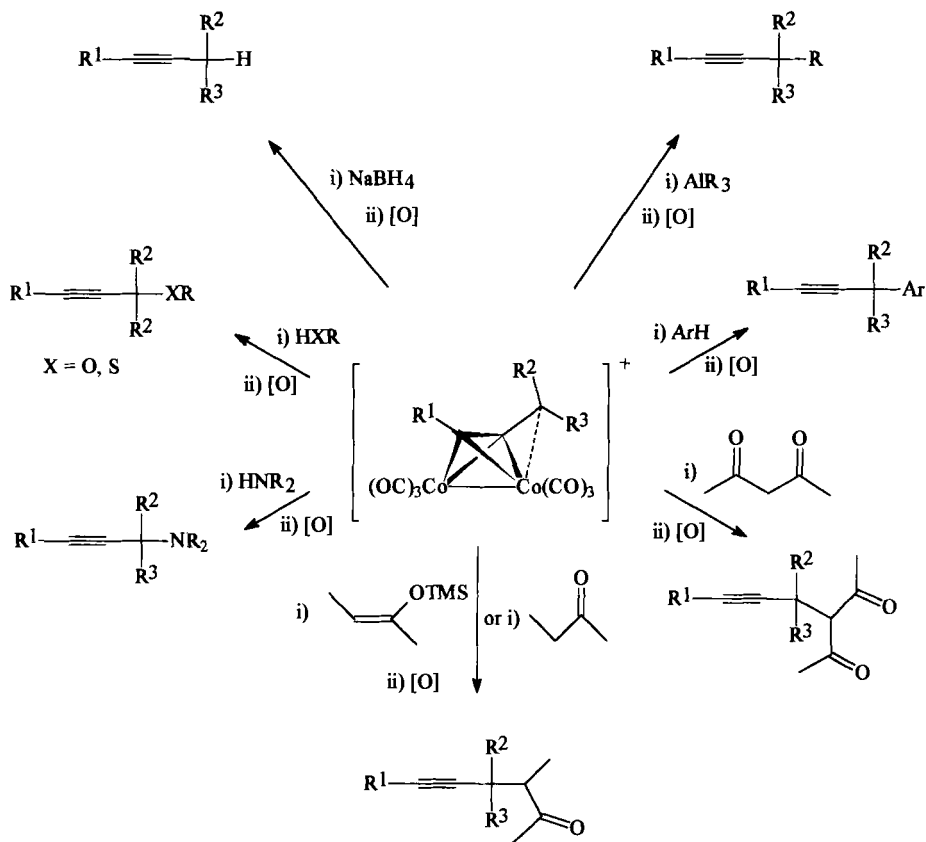
FIG. 13. The molecular structure of $[\text{Co}_2(\mu, \eta^2, \eta^2\text{-HC}_2\text{CH}_2\text{PEt}_3)(\text{CO})_6]^+$.

3. Reactions of Monocationic Species

The propargylic cations $[\text{Co}_2(\mu, \eta^2, \eta^3\text{-RC}_2\text{CR}_2)(\text{CO})_6]^+$ react as electrophiles with a variety of heteroatom- and carbon-centered nucleophiles to provide, following demetalation, propargylated products with complete regioselectivity. Complexation of the triple bond circumvents isomerization to allenic products. Reaction with asymmetrical ketones results in attack by the cation exclusively (>95%) at the more substituted α -carbon.^{72,74} (See Scheme 11.)

The stereochemical course of several $\text{Co}_2(\text{CO})_6$ -mediated reactions has been studied. For example, although alkynyl aldehydes undergo crossed aldol condensation with trimethylsilyl enol ethers with little stereoselectivity, their hexacarbonyldicobalt derivatives react with moderate to excellent *syn* diastereoselectivity.⁹⁶⁻¹⁰¹ The mechanism behind this selectivity has not been fully elucidated and is complicated by the fluxional nature of the intermediate cations. This stereoselective reaction has been successfully applied to the synthesis of β -lactam antibiotics.¹⁰⁰

Nicholas has studied a second generation of complexes with a chiral metal cluster obtained by substituting a CO ligand with a phosphine group (see Section II,C).⁶⁴ Thus, a mixture of diastereomeric alcohol complexes of the type $[\text{Co}_2(\mu, \eta^2, \eta^2\text{-RC}_2\text{CR}^1\text{R}^2\text{OH})(\text{CO})_5(\text{PPh}_3)]$ was prepared. Protonation of either isomer gives the same mixture (*syn/anti*) of the diastereomer cations $[\text{Co}_2(\mu, \eta^2, \eta^3\text{-RC}_2\text{CR}^1\text{R}^2)(\text{CO})_5(\text{PPh}_3)]^+$, where the major iso-

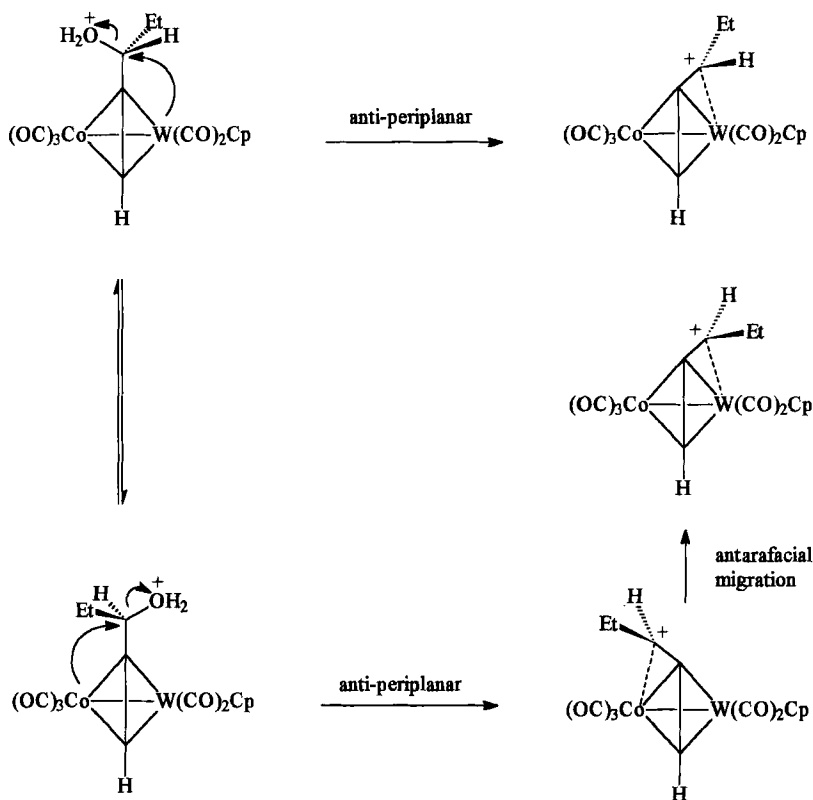


SCHEME 11.

mer adopts the *anti*-configuration as determined by NOE difference experiments; that is, the bulky substituent at the propargylic carbon is directed away from the phosphine ligand.¹⁰² Hence, the cations are formed diastereoselectively but not diastereospecifically. Monitoring some of the isomeric mixtures in acetone revealed a gradual change in the ratio of the isomers, approaching values of nearly one at equilibrium. The isomerization is a relatively high-energy process with an activation energy of 17–20 kcal mol⁻¹. Quenching of these cations, which are considerably less reactive than the $Co_2(CO)_6$ -stabilized systems, with oxygen nucleophiles showed moderate to complete stereoselectivity, suggesting kinetic control. However, the reactivity of this system was so reduced that reactions with carbon nucleophiles were unsuccessful. This problem can be overcome by using the bulky, weakly σ -donating, strongly π -accepting tris(1,1,1,3,3,3-hexafluoro-

oroisopropyl) phosphite ligand instead of triphenylphosphine to afford complexes that couple diastereoselectively with mild carbon nucleophiles; when the complexes are derived from enantio-enriched propargyl alcohols, the reactions occur with virtually complete enantioselectivity, resulting from the complete configurational stability of the cobalt cluster.¹⁰³

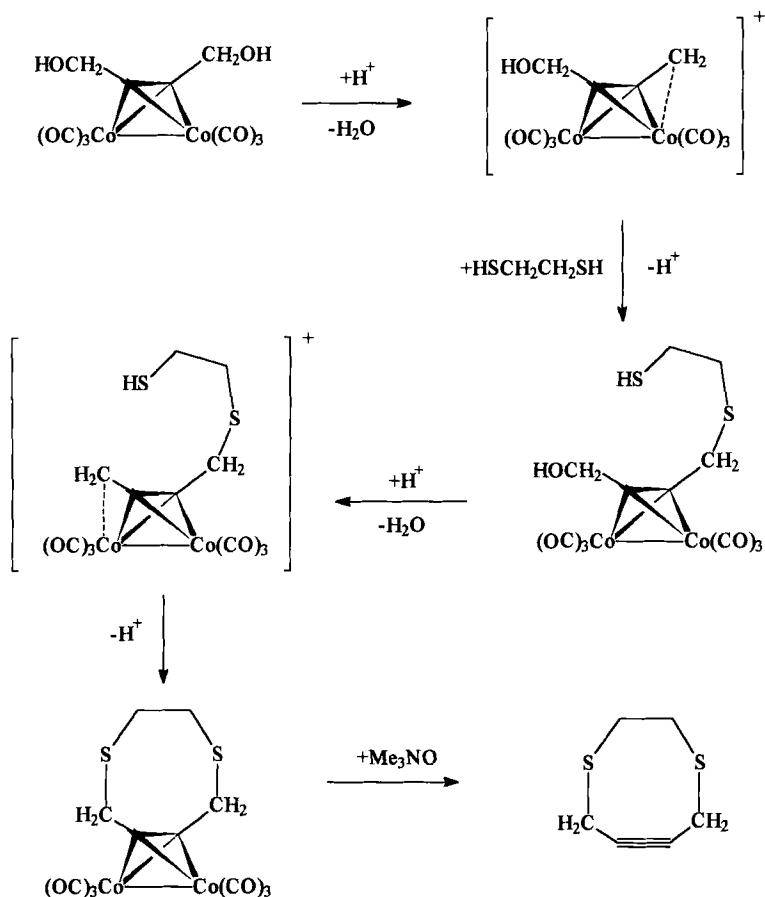
Another way to obtain chiral clusters is to use mixed-metal systems (see Section II,A). Addition of acid to one of the two diastereomers of $[\text{WCo}(\mu\text{-HC}_2\text{CH}(\text{OH})\text{Et})(\text{CO})_5\text{Cp}]$ leads to formation of two propargylium cations which do not isomerize in solution on the NMR time scale.⁷⁵ Similarly, protonation of the separate diastereomers of $[\text{MoCo}(\mu\text{-2-propynylborneol})(\text{CO})_5\text{Cp}]$ leads to formation of propargylium cations which are nonfluxional. It has been shown that the diastereomer ratios for metal-stabilized cationic clusters can be directly correlated with the ionization process, and it is proposed that the elimination of water is anchimerically assisted by



SCHEME 12.

the metal and proceeds through an anti-periplanar transition state (Scheme 12).¹⁰⁴ Detailed studies have been made of metal-mediated Wagner-Meerwein rearrangements in dicobalt, dimolybdenum, and cobalt-molybdenum complexes of the 2-fenchyl cation.¹⁰⁵

It is not always necessary to isolate the cobalt-stabilized cation, as in many cases it can be generated *in situ* by addition of acid, and some reactions can be performed with only a catalytic amount of acid present. An example is the reaction of $[\text{Co}_2(\mu\text{-HOCH}_2\text{C}_2\text{CH}_2\text{OH})(\text{CO})_6]$ with dithiols (Scheme 13) in which the thiol groups are sequentially added to the intermediate cations and each addition regenerates the acid.¹⁰⁶ The reaction also illustrates an intramolecular cyclization that utilizes distortion of the coordi-



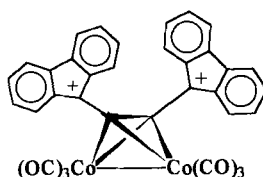
SCHEME 13.

nated alkyne to reduce the ring strain during the cyclization step. The bending associated with alkyne complexation has been employed by a number of research groups to facilitate the cyclization of acyclic alkynes.^{4,96,107,108}

The reactivity of $[\text{Co}_2(\mu, \eta^2, \eta^2\text{-HC}_2\text{CH}_2\text{SR}_2)(\text{CO})_6]^+$ is attenuated compared with that of $[\text{Co}_2(\mu, \eta^2, \eta^3\text{-HC}_2\text{CH}_2)(\text{CO})_6]^+$.⁷⁹ Kinetic data suggest that the reaction of $[\text{Co}_2(\mu, \eta^2, \eta^2\text{-HC}_2\text{CH}_2\text{SEt}_2)(\text{CO})_6]^+$ with MeOH proceeds via an $\text{S}_{\text{N}}2$ mechanism in which the SEt_2 molecule functions as a leaving group.

4. Synthesis of Dicationic Species

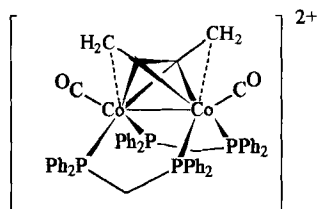
A metal-stabilized dicarbenium ion complex $[\text{Mo}_2(\text{H}_2\text{CC}_2\text{CH}_2)(\text{CO})_4\text{Cp}_2]^{2+}$ has been fully characterized and its structure determined by X-ray crystallography¹⁰⁹; however, the $[\text{Co}_2(\text{H}_2\text{CC}_2\text{CH}_2)(\text{CO})_6]^{2+}$ dication has not been isolated, possibly because of the poorer ability of $\text{Co}(\text{CO})_3$ to stabilize positive charge. A bis(9-fluorenyl)ethyne ditetrafluoroborate-ethyne-hexacarbonyldicobalt complex **29** has been reported, but is unstable at room temperature.¹¹⁰ (See Formula 29.)



29

FORMULA 29.

The species $[\text{Co}_2(\text{H}_2\text{CC}_2\text{CH}_2)(\text{CO})_6]^{2+}$ has been postulated as an intermediate in a number of reactions. For example, reaction of $[\text{Co}_2(\mu\text{-HOCH}_2\text{C}_2\text{H}_4\text{OH})(\text{CO})_6]$ with a large excess of $\text{HBF}_4 \cdot \text{OEt}_2$ at -50°C affords a red oil that, when treated with HNPh_2 , affords a mixture containing $[\text{Co}_2(\mu\text{-Ph}_2\text{NCH}_2\text{C}_2\text{H}_4\text{NPh}_2)(\text{CO})_6]$ as one of the products.¹¹¹ However, the ability of the dicobalt unit to stabilize positive charge can be improved by substitution with phosphine ligands.¹¹¹ Protonation of $[\text{Co}_2(\mu\text{-HOCH}_2\text{C}_2\text{H}_4\text{OH})(\mu\text{-dppm})_2(\text{CO})_2]$ with $\text{HBF}_4 \cdot \text{OEt}_2$ affords $[\text{Co}_2(\mu\text{-H}_2\text{CC}_2\text{CH}_2)(\mu\text{-dppm})_2(\text{CO})_2][\text{BF}_4]_2$ (**30**), which is nonfluxional on the NMR time scale at room temperature. (See Formula 30.)



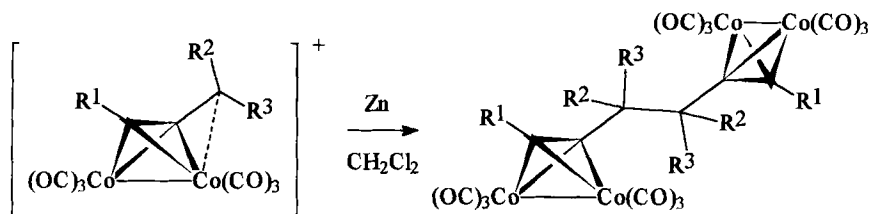
30

FORMULA 30.

Alternatively, nucleophiles can be used to stabilize dication species in a manner similar to the monocationic species. Protonation of $[\text{Co}_2(\mu\text{-HOCH}_2\text{C}_2\text{CH}_2\text{OH})(\text{CO})_6]$ in SMe_2 with $\text{HBF}_4 \cdot \text{OEt}_2$ affords $[\text{Co}_2(\mu\text{-Me}_2\text{SCH}_2\text{C}_2\text{CH}_2\text{SMe}_2)(\text{CO})_6][\text{BF}_4]_2$ in high yield as a thermally stable orange solid. It behaves as a source of $[\text{Co}_2(\text{H}_2\text{CC}_2\text{CH}_2)(\text{CO})_6]^{2+}$ in its reactions with HNPh_2 , HNEt_2 , and HSEt , which afford $[\text{Co}_2(\mu\text{-Ph}_2\text{NCH}_2\text{C}_2\text{CH}_2\text{NPh}_2)(\text{CO})_6]$, $[\text{Co}_2(\mu\text{-Et}_2\text{NCH}_2\text{C}_2\text{CH}_2\text{NEt}_2)(\text{CO})_6]$, and $[\text{Co}_2(\mu\text{-EtSCH}_2\text{C}_2\text{CH}_2\text{SEt})(\text{CO})_6]$, respectively.¹¹¹ There are several examples of double Nicholas reactions which occur without isolation of dicationic intermediates, as already illustrated in Scheme 13.^{106,112-116}

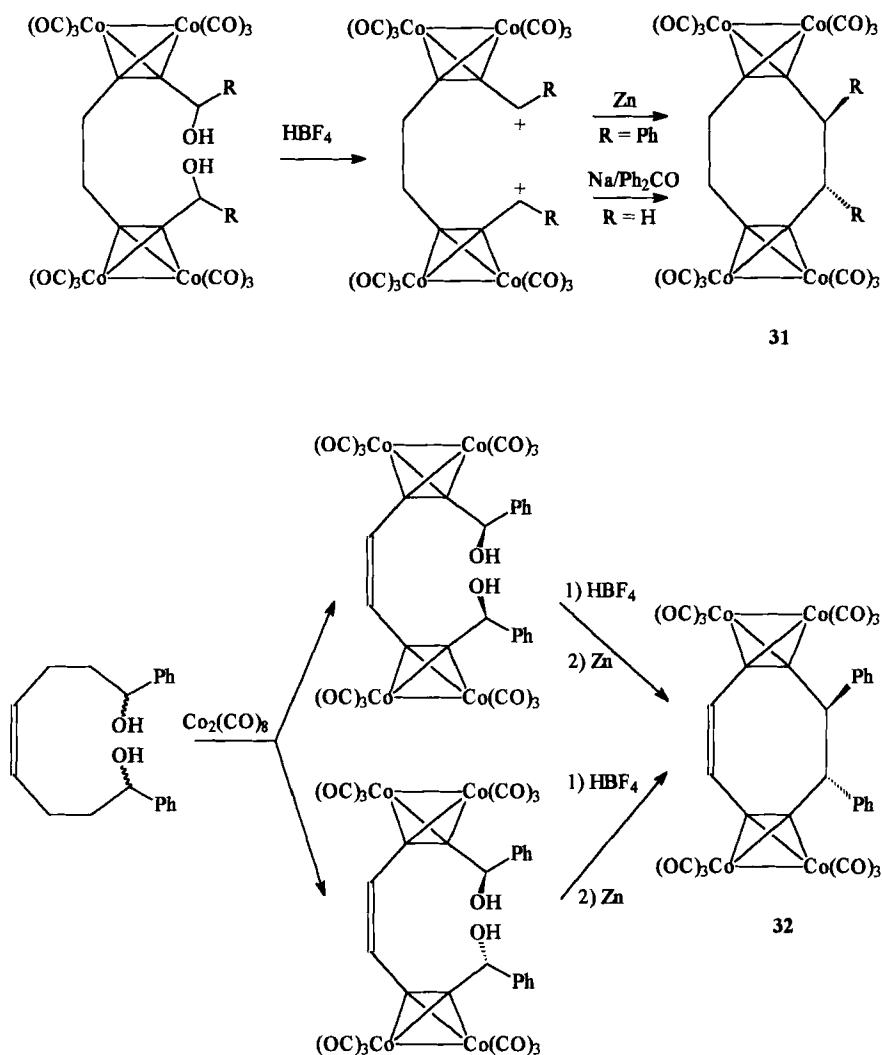
E. Radical Species

$\text{Co}_2(\text{CO})_6$ -complexed propargyl cations were known for some time before $\text{Co}_2(\text{CO})_6$ -complexed propargyl radicals were studied.¹¹⁷ These radicals were first postulated as intermediates in the reactions of propargyl halides with $[\text{Co}_2(\text{CO})_8]^{118}$ and in some coupling reactions of $[\text{Co}_2(\mu, \eta^2, \eta^3\text{-HC}_2\text{CHPh})(\text{CO})_6]^+$.¹¹⁹ They have been implicated in manganese-promoted cyclocondensation reactions.¹²⁰ Radical intermediates are conveniently generated by the reduction of the corresponding cations with zinc, as shown in Eq. (11).¹¹⁷



(11)

Primary cations give both coupled and H-atom abstraction products. Secondary cations undergo coupling only, whereas tertiary cations with methyl substituents show only H-atom abstraction and electrophilic coupling. The intramolecular variant of this reaction is particularly useful for the efficient synthesis of medium-sized 1,5-diynes and has been applied to the synthesis of hexacarbonyldicobalt-complexed 1,5-cyclooctadiynes **31** and a cyclooct-5-ene-1,5-diyne derivative **32** (Scheme 14).¹²¹ The eight-membered rings



SCHEME 14.

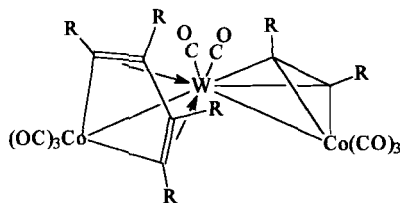
are formed with high *dl*-diastereoselectivity (*de* > 98%). Use of Na/Ph₂CO in benzene as an alternative reducing agent to Zn has the advantage that it excludes H-atom abstraction. The cyclic ene-diyne complex **32** is produced as the single *dl*-isomer (*de* > 99%) by starting from either isomer of the diol.

III

TRINUCLEAR CLUSTERS

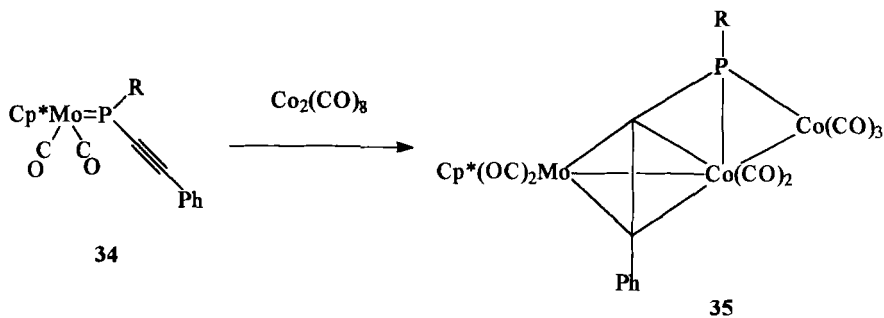
Alkyne-substituted transition metal clusters have been reviewed,^{122,123} and other reviews of interest have discussed cyclopentadienyl metal clusters of group 9 transition metals¹²⁴ and hydrocarbyl ligand derivatives of group 6 through group 9 heterometallic clusters.¹²⁵

Three metals can form either open-chain 50 cluster-valence electron or, more commonly, triangular 48 cluster-valence electron frameworks. Reaction of the compounds [W(C₂R₂)₃(CO)] (R = Et or Pr) with [Co₂(CO)₈] affords the open-chain trinuclear clusters [WCo₂(μ-RC₂R)(μ-C₄R₄)(CO)₈] (**33**) in which one cobalt-tungsten bond is bridged by a perpendicularly coordinated alkyne in a manner similar to dinuclear complexes, whereas the second cobalt-tungsten bond is bridged by an alkyne-derived butadiene ligand¹²⁶ (see Formula 33). Reaction of **34**, illustrated in Eq. (12), with [Co₂(CO)₈] affords the open-chain trinuclear complex **35**.¹²⁷



33

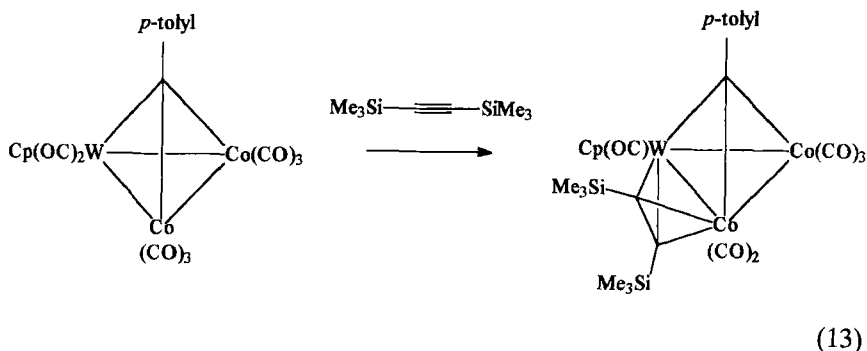
FORMULA 33.



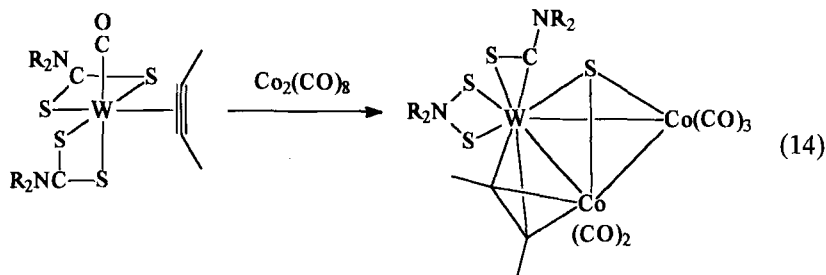
35

(12)

Triangular trinuclear systems in which the alkyne bridges two of the three metals have been prepared by reaction of preformed clusters with alkynes, as in Eq. (13),¹²⁸



or by addition of $[\text{Co}_2(\text{CO})_8]$ to an alkyne-containing precursor, as illustrated in Eq. (14).¹²⁹



More commonly, the alkyne bonds simultaneously to all three metals in triangular clusters in a parallel bonding mode in which the alkyne is σ -bonded to two metals and π -bonded to the third metal. The examples of tricobalt-alkyne clusters are based on CoCp fragments.¹²⁴ A wide variety of monoalkynes, diynes, and functionalized alkynes can be introduced into the trinuclear framework of the unsaturated cluster complex $[\text{Co}_3(\mu_2\text{-CO})_2\text{Cp}_3]$ to form the clusters $[\text{Co}_3(\mu\text{-CO})(\mu\text{-alkyne})\text{Cp}_3]$.^{130,131} The complexes can exist as two isomers with the $\mu\text{-CO}$ either edge bridging or face capping. The structure of a face bridging cluster $[\text{Co}_3(\mu_3\text{-CO})(\mu\text{-F}_3\text{CC}_2\text{CF}_3)\text{Cp}_3]$ is shown in Fig. 14.¹³¹ The alkyne is orientated parallel to one cobalt-cobalt edge and offset toward the unique cobalt atom.

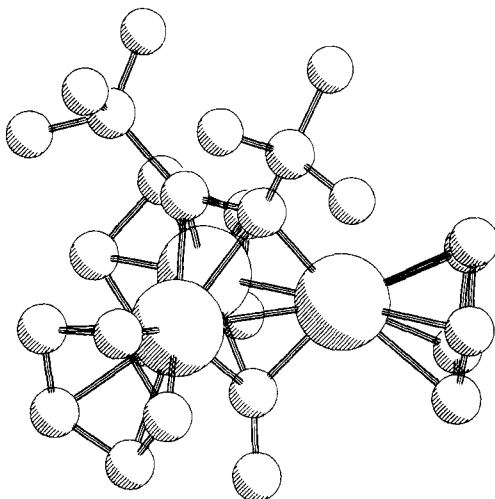
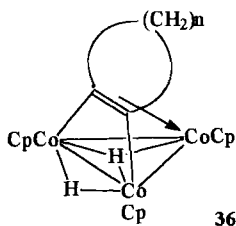


FIG. 14. The molecular structure of $[\text{Co}_3(\mu_3\text{-CO})(\mu\text{-F}_3\text{CC}_2\text{CF}_3)\text{Cp}_3]$.

Reaction of $[\text{Co}(\text{H}_2\text{C}=\text{CH}_2)_2\text{Cp}]$ with the unsaturated dinuclear complex $[\text{Co}_2(\mu\text{-Me}_3\text{SiC}_2\text{SiMe}_3)\text{Cp}_2]$ (**3**) results in addition of a CoCp fragment to afford the trinuclear cluster $[\text{Co}_3(\mu\text{-Me}_3\text{SiC}_2\text{SiMe}_3)\text{Cp}_3]$, which, when exposed to carbon monoxide, forms $[\text{Co}_3(\mu_3\text{-CO})(\mu\text{-Me}_3\text{SiC}_2\text{SiMe}_3)\text{Cp}_3]$.¹² Thermolysis of either $[\text{Co}_3(\mu\text{-Me}_3\text{SiC}_2\text{SiMe}_3)\text{Cp}_3]$ or $[\text{Co}_3(\mu_3\text{-CO})(\mu\text{-Me}_3\text{SiC}_2\text{SiMe}_3)\text{Cp}_3]$ results in carbon-carbon bond cleavage and formation of the bis-alkylidyne cluster $[\text{Co}_3(\mu_3\text{-CSiMe}_3)_2\text{Cp}_3]$.

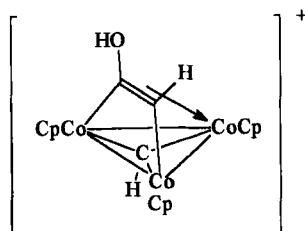
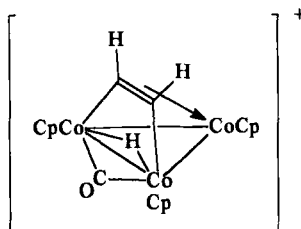
Alkyne hydrido cluster complexes of the type $[\text{Co}_3(\mu\text{-H})_2(\mu\text{-alkyne})\text{Cp}_3]$ can be prepared by 1,2 double C-H activation of alkenes.^{132,133} For example, the μ -cycloalkyne complexes **36** can be prepared either from the respective cycloalkenes and $[\text{Co}(\text{C}_2\text{H}_4)_2\text{Cp}]$ or by using the reductive cleavage of cobaltocene with potassium as a source of CpCo fragments. (See Formula 36.)



$$n = 3, 4, 5, 6$$

FORMULA 36.

The bis(methylidyne)hydridotricobalt cluster $[\text{Co}_3(\mu\text{-H})(\mu_3\text{-CH})_2\text{Cp}_3]^+$ reacts with carbon monoxide to form **37** by coupling of a HOC^+ fragment with a cluster-bound methylidyne ligand.¹³⁴ Carbon monoxide deinsertion and methylidyne–methylidyne coupling occur when **37** is treated with carbon monoxide under pressure to afford **38**. (See Formulae 37 and 38.)

**37****38**

FORMULAE 37 and 38.

Mixed-metal triangular alkyne clusters containing cobalt also favor the parallel, as opposed to the perpendicular, alkyne coordination mode. Reaction of $[\text{HFeCo}_3(\text{CO})_{12}]$ with 3-hexyne affords $[\text{FeCo}_2(\mu\text{-EtC}_2\text{Et})(\text{CO})_9]$ as the major product.¹³⁵ Substitution of a carbonyl ligand for a phosphine ligand in $[\text{FeCo}_2(\mu\text{-EtC}_2\text{Et})(\text{CO})_9]$ occurs at a cobalt center and induces a reorientation of the alkyne moiety, as has been demonstrated by the structure of $[\text{FeCo}_2(\mu\text{-EtC}_2\text{Et})(\text{PPh}_3)(\text{CO})_8]$.¹³⁶ In the precursor the alkyne is σ -bonded to the cobalt atoms and π -bonded to the iron atom, whereas in the product the alkyne is σ -bonded to a cobalt and an iron atom and π -bonded to the cobalt atom bearing the phosphine ligand (Fig. 15). Reaction of $\text{NEt}_4[\text{RuCo}_3(\mu_4\text{-}\eta^2\text{-PhC}_2\text{Ph})(\mu\text{-CO})_2(\text{CO})_8]$ (see Section IV) with HCl affords the analogous ruthenium-containing cluster $[\text{RuCo}_2(\mu_3\text{-}\eta^2\text{-PhC}_2\text{Ph})(\text{CO})_9]$.¹³⁷ Alternatively, clusters of this type, in which the alkyne is in a parallel orientation π -bound to a cobalt center, can be prepared by the reaction of $[\text{RuCo}_2(\text{CO})_{11}]$ with alkynes.^{138–140} For $[\text{RuCo}_2(\mu\text{-alkyne})(\text{CO})_9]$ clusters, kinetically favored cobalt–carbonyl and thermodynamically favored ruthenium–carbonyl phosphine-substituted products have

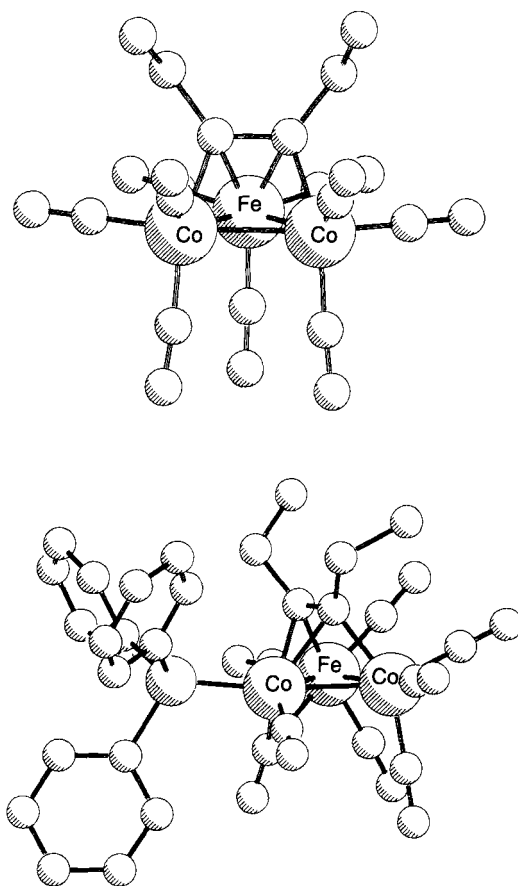
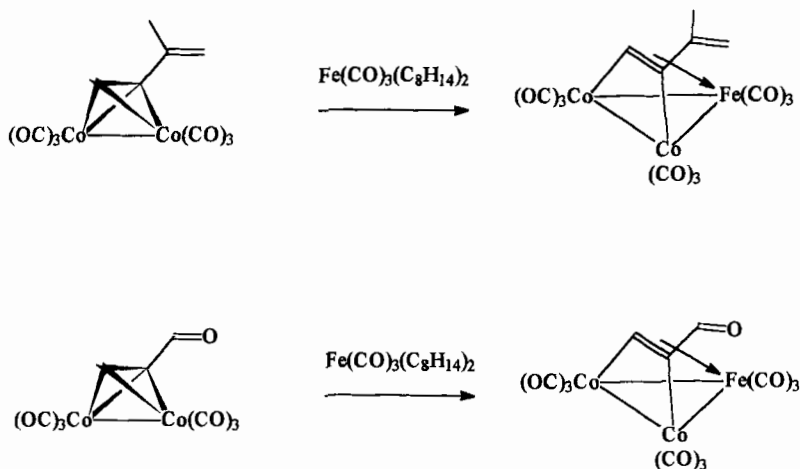


FIG. 15. The molecular structures of $[\text{FeCo}_2(\mu\text{-EtC}_2\text{Et})(\text{CO})_9]$ and $[\text{FeCo}_2(\mu\text{-EtC}_2\text{Et})(\text{PPh}_3)(\text{CO})_8]$.

been isolated.¹⁴¹ Competition reactions between $[\text{FeCo}_2(\mu\text{-MeC}_2\text{Me})(\text{CO})_9]$, $[\text{RuCo}_2(\mu\text{-MeC}_2\text{Me})(\text{CO})_9]$, and PPh_3 demonstrate a higher substitutional lability of the iron-containing cluster and phosphine transfer from the iron- to the ruthenium-containing cluster.

Reaction of hexacarbonyldicobalt complexes of ene-yne or hetero-ene-yne with (biscyclooctene)(tricarbonyl)iron results in formation of $[\text{FeCo}_2(\mu\text{-alkyne})(\text{CO})_9]$ (Scheme 15).¹⁴² In both cases the free double bond in the vicinity of the Co_2C_2 unit facilitates the incorporation of the incoming $\text{Fe}(\text{CO})_3$ fragment.

Reaction of excess $[\text{Fe}_2(\text{CO})_9]$ or $[\text{Ru}(\text{CO})_5]$ or $[\text{Os}(\text{CO})_5]$ with $[\text{NiCo}(\mu\text{-R}^1\text{C}_2\text{R}^2)(\text{CO})_3\text{Cp}]$ ($\text{R}^1 = \text{R}^2 = \text{Ph}$, Et ; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$) affords the



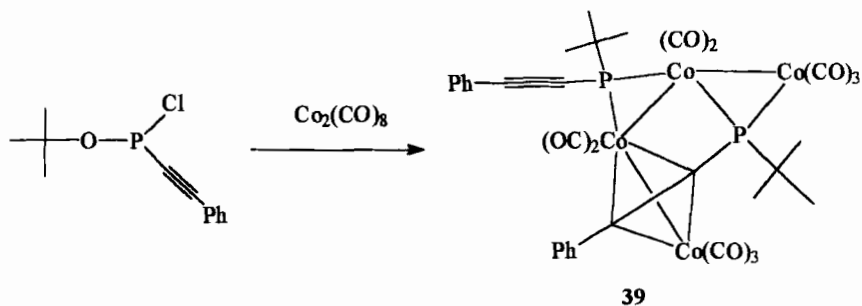
SCHEME 15.

heterotrimetallic clusters $[\text{NiCoM}(\text{R}^1\text{C}_2\text{R}^2)(\text{CO})_6\text{Cp}]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$).^{143,144} In all the examples that have been structurally characterized, the alkyne is oriented parallel to one edge of the triangular framework, but the particular location varies. Mixed-metal systems of the type $\text{CoM}'\text{M}''(\mu\text{-alkyne})$ can also be prepared by metal exchange reactions.¹⁴⁵

IV

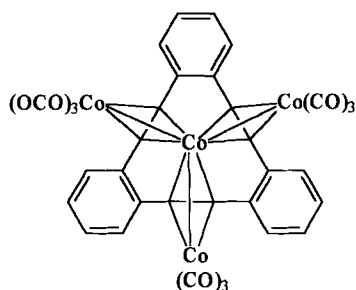
TETRANUCLEAR COMPLEXES

Tetranuclear alkyne clusters involving cobalt can adopt a variety of geometries. Reductive dehalogenation of $(^t\text{Bu})(\text{PhC}\equiv\text{C})\text{PCl}$ by $[\text{Co}_2(\text{CO})_8]$ affords **39** in which a chain of four cobalt centers is supported by the functionalized alkyne, as shown in Eq. (15).^{146,147}



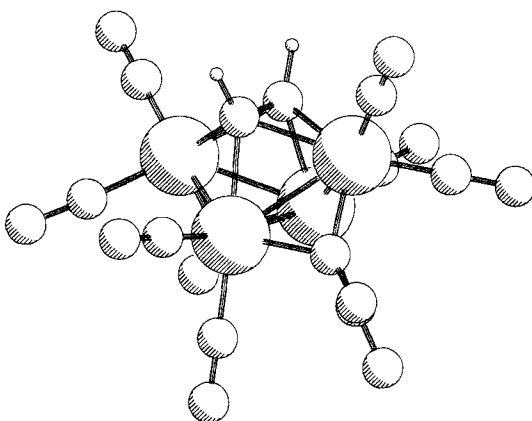
(15)

An interesting tetracobalt cluster **40** in which three alkyne functionalities are simultaneously coordinated has been prepared by the reaction of $[\text{Co}_2(\text{CO})_8]$ with tribenzocyclyne¹⁴⁸ (see Formula 40). Reaction of $[\text{Co}_3(\mu_3\text{-S})(\text{CO})_9]$ with Me_3NO , CO , and $\text{PhC}\equiv\text{CH}$ affords $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-PhC}_2\text{H})(\mu_4\text{-S})(\mu\text{-CO})_2(\text{CO})_8]$, which has a rectangular Co_4 skeleton to which quadruply bridging sulfur and ligands are coordinated on opposite sides.¹⁴⁹ The tetrahedral cluster $[\text{Mo}_2\text{Co}_2(\mu_3\text{-S})_3(\text{CO})_4\text{Cp}'_2]$ reacts with $\text{PhC}\equiv\text{CH}$ to afford $[\text{Mo}_2\text{Co}_2(\mu_3\text{-}\eta^2\text{-PhC}_2\text{H})(\mu_3\text{-S})_3(\text{CO})_2\text{Cp}'_2]$, which is also tetrahedral with the $\mu_3\text{-}\eta^2\text{-PhC}_2\text{H}$ ligand bound to a Co_2Mo face, as is common in trinuclear clusters (see Section III).¹⁵⁰

**40**

FORMULA 40.

The majority of tetranuclear alkyne clusters containing cobalt adopt butterfly geometries.^{151,152} This is illustrated by the molecular structure of $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-HC}_2\text{H})(\mu\text{-CO})_2(\text{CO})_8]$ (Fig. 16), which can be prepared by the

FIG. 16. The molecular structure of $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-HC}_2\text{H})(\mu\text{-CO})_2(\text{CO})_8]$.

reaction of $[\text{Co}_4(\text{CO})_{12}]$ with acetylene.¹⁵³ The alkyne lies parallel to the hinge bond and is bonded to all four cobalt atoms. If the alkyne is regarded as a four-electron donor, this type of compound has 60 cluster valence electrons and is therefore formally electron deficient, as the predicted value for a butterfly geometry is 62 electrons. However, an alternative view is to regard the alkyne as two 3-electron donor methylidyne units, in which case the electron count is 62 in accord with a *closo*-octahedral cluster. A detailed vibrational study has been made of $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-HC}_2\text{H})(\mu\text{-CO})_2(\text{CO})_8]$. Comparison of the coordinated acetylene frequencies and those of acetylene adsorbed on a transition-metal surface shows good correspondence.¹⁵³ Phosphine substitution of $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-HC}_2\text{H})(\mu\text{-CO})_2(\text{CO})_8]$ affords the disubstituted cluster, $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-HC}_2\text{H})(\mu\text{-CO})_2(\text{PPh}_3)_2(\text{CO})_6]$, in which the phosphines are coordinated to the wing-tip cobalt atoms.¹⁵⁴

Complexes of the type $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-alkyne})(\mu\text{-CO})(\text{CO})_4\text{Cp}_2]$, illustrated by the molecular structure of $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-CO})(\text{CO})_4\text{Cp}_2]$ (Fig. 17),¹⁵⁵ can be prepared by the reaction of $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ with $[\text{Co}(\text{CO})_2\text{Cp}]$.¹⁵⁶

Stepwise coordination by phosphinoalkynes has also been used to build up butterfly clusters. For example, reaction of $[\text{Co}_2(\mu\text{-MeC}\equiv\text{CMe})(\text{CO})_6]$ and $\text{Ph}_2\text{PC}\equiv\text{CPh}$ affords $[\text{Co}_2(\mu\text{-MeC}\equiv\text{CMe})(\eta^1\text{-Ph}_2\text{PC}\equiv\text{CPh})(\text{CO})_5]$ (**41**), which reacts with $[\text{Co}_2(\text{CO})_8]$ to afford $[\text{Co}_2(\mu\text{-MeC}\equiv\text{CMe})(\text{CO})_5(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC}\equiv\text{CPh})\text{Co}_2(\text{CO})_6]$ (**42**), which upon thermolysis rearranges to give the butterfly tetracobalt cluster **43** illustrated in Scheme 16.¹⁵⁷

A variety of cobalt-containing mixed-metal butterfly alkyne clusters are known and will be described in approximate order of decreasing cobalt content. The dehalogenation of $[\text{RuCl}_2(\text{Ph}_2\text{PC}\equiv\text{CBu}^i)(p\text{-cymene})]$ by $[\text{Co}_2(\text{CO})_8]$ followed by protonation affords $[\text{RuCo}_3(\mu_4\text{-}\eta^2\text{-Bu}^i\text{C}_2\text{H})(\mu\text{-CO})(\text{CO})_4\text{Cp}_2]$.

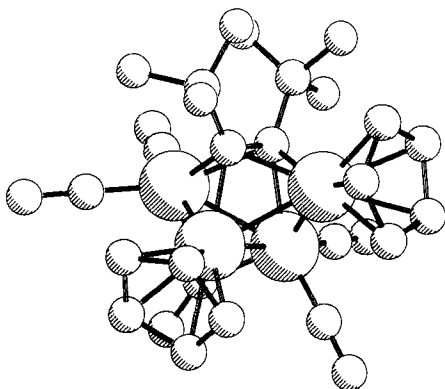
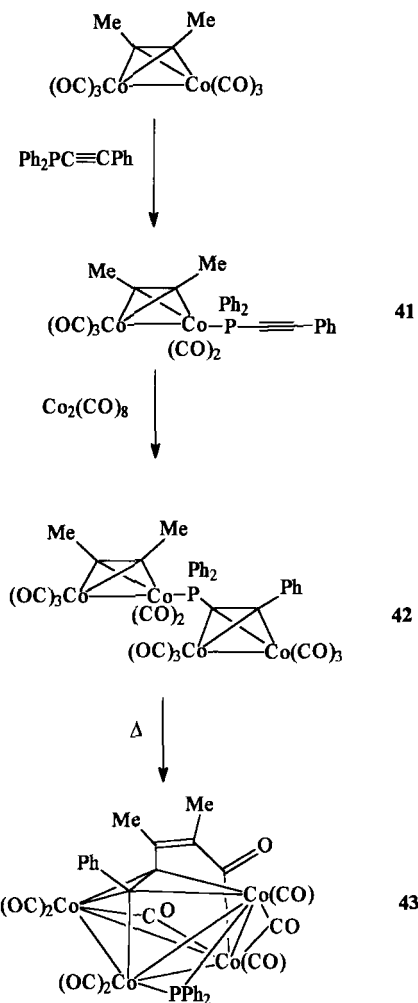


FIG. 17. The molecular structure of $[\text{Co}_4(\mu_4\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-CO})(\text{CO})_4\text{Cp}_2]$.



SCHEME 16.

$\text{PPh}_2)(\text{CO})_9]$.¹⁵⁸ The ruthenium atom occupies a hinge position and the phosphido group bridges between the ruthenium and a wing-tip cobalt atom. Reaction of the tetrahedral cluster $[\text{Co}_3\text{Mo}(\text{CO})_{11}\text{Cp}']$ with $\text{PhC}\equiv\text{CH}$ results in insertion into a cobalt–molybdenum bond to afford $[\text{Co}_3\text{Mo}(\mu_4\text{-}\eta^2\text{-PhC}_2\text{H})(\text{CO})_9\text{Cp}']$, in which the molybdenum atom occupies a wing-tip position.¹⁵⁹ Similar reaction of the analogous tungsten-containing cluster $[\text{Co}_3\text{W}(\text{CO})_{11}\text{Cp}']$ with $\text{PhC}\equiv\text{CH}$ results in cluster fragmentation.

However, $[\text{Co}_2\text{W}_2(\mu\text{-CO})_3(\text{CO})_7\text{Cp}'_2]$ reacts with $\text{PhC}\equiv\text{CH}$ to afford $[\text{Co}_2\text{W}_2(\mu_4\text{-}\eta^2\text{-PhC}_2\text{H})(\text{CO})_8\text{Cp}'_2]$.¹⁵⁹ The analogous molybdenum-containing cluster $[\text{Co}_2\text{Mo}_2(\mu_4\text{-}\eta^2\text{-MeC}_2\text{Me})(\text{CO})_8\text{Cp}_2]$ has been characterized by X-ray crystallography and contains the cobalt atoms in the hinge positions.^{160,161} Treatment of $\text{NEt}_4[\text{RuCo}_3(\text{CO})_{12}]$ with excess $\text{PhC}\equiv\text{CPh}$ affords $\text{NEt}_4[\text{RuCo}_3(\mu_4\text{-}\eta^2\text{-PhC}_2\text{Ph})(\mu\text{-CO})_2(\text{CO})_8]$, which contains a ruthenium atom in a hinge position.¹³⁷ The nitrosyl-substituted cluster $[\text{RuCo}_3(\text{CO})_{11}(\text{NO})]$ reacts with alkynes via insertion into a cobalt–cobalt bond to afford the butterfly clusters $[\text{RuCo}_3(\mu_4\text{-}\eta^2\text{-alkyne})(\text{CO})_9(\text{NO})]$, in which the ruthenium atom occupies a hinge position and the nitrosyl ligand is attached to a wing-tip cobalt atom.¹⁶² Cluster fragmentation is also observed during the reaction, and small amounts of $[\text{RuCo}_2(\mu_3\text{-}\eta^2\text{-alkyne})(\text{CO})_9]$ are also produced. Reaction of $[\text{RhCo}_3(\text{CO})_{12}]$ with $\text{PhC}\equiv\text{CPh}$ yields two butterfly clusters. The first, $[\text{RhCo}_3(\mu_4\text{-}\eta^2\text{-PhC}_2\text{Ph})(\text{CO})_{10}]$, is formed by alkyne insertion into the tetrahedral framework, whereas formation of the second cluster, $[\text{Rh}_2\text{Co}_2(\mu_4\text{-}\eta^2\text{-PhC}_2\text{Ph})(\text{CO})_{10}]$, involves metal exchange.¹⁶³ The second cluster can also be prepared directly from $[\text{Rh}_2\text{Co}_2(\text{CO})_{12}]$ and the alkyne.²⁶ The rhodium atoms occupy the hinge positions and are the sites of phosphine substitution.¹⁶⁴ Reaction of $[\text{Ru}_2\text{Co}_2(\text{CO})_{13}]$ with alkynes leads to insertion of the alkyne into the cobalt–cobalt bond.¹⁶⁵ A Ru_2Co_2 butterfly cluster is also formed by the reaction of $[\text{Co}_2(\text{CO})_8]$ with $[\text{Ru}_2(\mu\text{-PhC}_2\text{Ph})(\mu\text{-CO})\text{Cp}_2]$, and again the cobalt atoms occupy the wing-tip positions.¹⁶⁶

Reaction of hexacarbonyldicobalt internal alkyne complexes with $[\text{Fe}_2(\text{CO})_4\text{Cp}_2]$ affords the butterfly clusters $[\text{Co}_2\text{Fe}_2(\mu_4\text{-}\eta^2\text{-alkyne})(\mu_3\text{-CO})_2(\text{CO})_4\text{Cp}_2]$ and $[\text{CoFe}_3(\mu_4\text{-}\eta^2\text{-alkyne})(\mu_3\text{-CO})_2(\text{CO})_2\text{Cp}_3]$.^{167,168} Similarly, butterfly clusters are formed upon reaction of hexacarbonylalkyne–dicobalt complexes with $[\text{Mo}_2(\mu\text{-SMe})_2(\text{CO})_2\text{Cp}_2]$.¹⁶⁹ The products $[\text{Co}_2\text{Mo}_2(\mu_4\text{-}\eta^2\text{-alkyne})(\mu_3\text{-S})_2(\text{CO})_4\text{Cp}_2]$ have cobalt atoms at the wing-tip positions and sulfur atoms capping the Mo_2Co faces. A butterfly cluster of a different type is produced by the reaction of the tetrahedral cluster $[\text{Pt}_2\text{Co}_2(\text{CO})_8(\text{COD})]$ with $\text{EtC}\equiv\text{CEt}$. The product contains two alkynes triply bridging Pt_2Co faces, and the two platinum atoms in the hinge positions are joined by a short $\text{Pt}\text{—}\text{Pt}$ bond (Fig. 18).¹⁷⁰

Cluster expansion of vinylidene-bridged triangular FeCo_2 or RuCo_2 clusters with $[\text{Rh}(\text{CO})_2\text{Cp}]$ building blocks affords FeCo_2Rh and RuCo_2Rh butterfly alkyne clusters which exist as two isomers with either both cobalt atoms or a cobalt atom and an iron atom in the wing-tip positions.¹⁷¹ Carbonyl transfer allows interconversion with butterfly vinylidene clusters.¹⁷¹ Cluster expansion of a range of mixed-metal trinuclear alkyne clusters by addition of $\text{Fe}(\text{CO})_3$ and RhCp fragments also affords tetranuclear alkyne butterfly clusters.¹⁷² Again, framework isomerism is observed, and

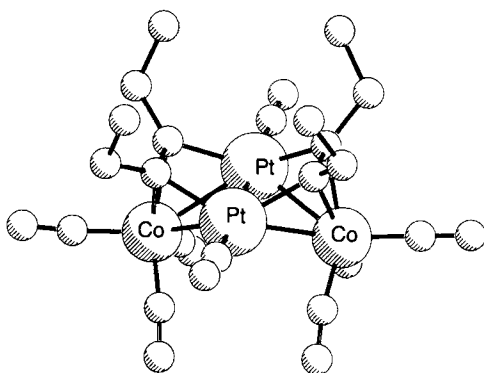


FIG. 18. The molecular structure of $[\text{Pt}_2\text{Co}_2(\mu\text{-EtC}_2\text{Et})_2(\text{CO})_8]$.

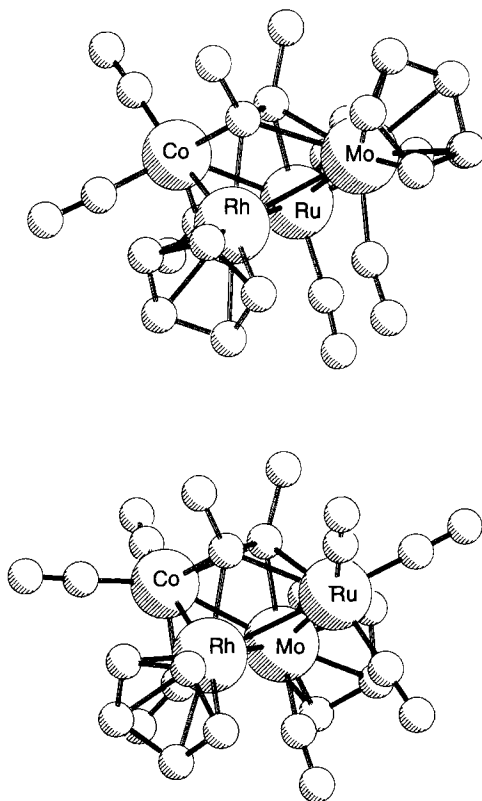


FIG. 19. The molecular structures of two isomers of $[\text{RuCoMoRh}(\mu_4\text{-}\eta^2\text{-MeC}_2\text{Me})(\mu\text{-CO})_2(\text{CO})_5\text{Cp}_2]$.

two isomers of $[\text{RuCoMoRh}(\mu_4\text{-}\eta^2\text{-MeC}_2\text{Me})(\mu\text{-CO})_2(\text{CO})_5\text{Cp}_2]$ have been structurally characterized (Fig. 19). Both are butterfly clusters with a wing-tip cobalt atom and a hinge rhodium atom, but they differ in the sites occupied by the molybdenum and ruthenium centers. Reaction of $[\text{PPN}][\text{CoRu}_3(\text{CO})_{13}]$ with $\text{PhC}\equiv\text{CPh}$ affords the butterfly cluster $[\text{CoRu}_3(\mu_4\text{-}\eta^2\text{-PhC}_2\text{Ph})(\mu\text{-CO})_2(\text{CO})_9]$ in which the cobalt center is in a wing-tip site.¹⁷³ Cluster expansion of $[\text{Fe}_3(\mu_3\text{-CF})_2(\text{CO})_9]$ by reaction with $[\text{Co}(\text{CO})_2\text{Cp}^*]$ results in carbon-carbon bond formation and isolation of the butterfly cluster $[\text{CoFe}_3(\mu_4\text{-}\eta^2\text{-FC}_2\text{F})(\text{CO})_9\text{Cp}^*]$ containing difluoroethyne and a wing-tip cobalt atom.¹⁷⁴

V

HIGHER NUCLEARITY COMPLEXES

There are few high-nuclearity alkyne clusters, and those that are known are mainly homonuclear osmium clusters.¹²³ Reaction of the tetrahedral cluster $[\text{Pt}_2\text{Co}_2(\text{CO})_8(\text{COD})]$ with $\text{PhC}\equiv\text{CPh}$ affords $[\text{Pt}_3\text{Co}_2(\mu_3\text{-PhC}_2\text{Ph})(\text{CO})_6(\text{COD})_2]$, which contains a bow-tie cluster of three platinum atoms and two cobalt atoms with a platinum atom in the center. The PhC_2Ph ligands bridge the two triangular Pt_2Co groupings in parallel bonding modes (Fig. 20).¹⁷⁰

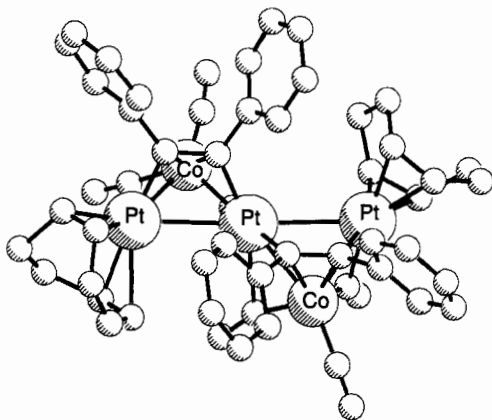
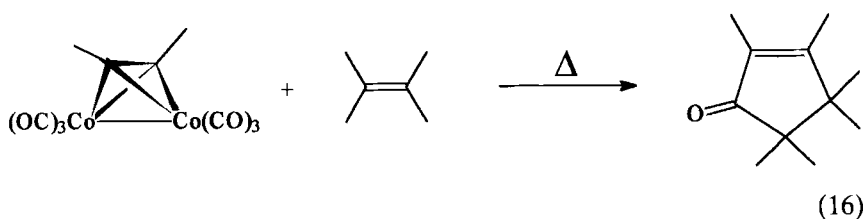


FIG. 20. The molecular structure of $[\text{Pt}_3\text{Co}_2(\mu_3\text{-PhC}_2\text{Ph})(\text{CO})_6(\text{COD})_2]$.

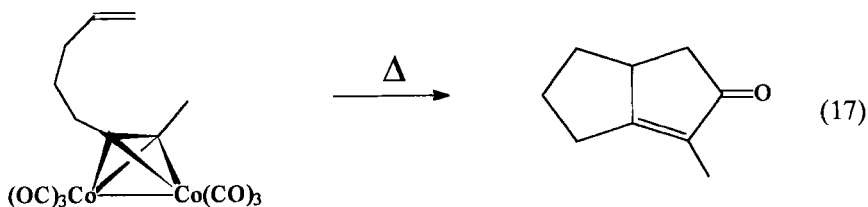
VI

APPLICATIONS

This review has already indicated numerous applications of dicobalt-alkyne complexes in organic synthesis. Like the Nicholas reaction (see Section II,D), the Pauson-Khand reaction has seen widespread use.¹⁷⁵ This reaction is a three-component cycloaddition of alkynes with alkenes and carbon monoxide which occurs in the presence of octacarbonyldicobalt to afford cyclopentenones, as shown in Eq. (16).



Sufficient information about the reaction has been gathered to allow fairly accurate predictions of yield as well as of stereo- and regioselectivity.^{176,177} The reaction proceeds via the formation of hexacarbonylalkyne-dicobalt complexes and is remarkably tolerant of functional groups in both the alkyne and the alkene. The intramolecular Pauson-Khand reaction is an effective way of preparing bi- and polycyclic systems, and the cyclization of 1,6-heptynyne derivatives to give bicyclo[3.3.0]oct-1-en-3-ones has been the most popular application of the Pauson-Khand reaction in natural product synthesis [Eq. (17)].

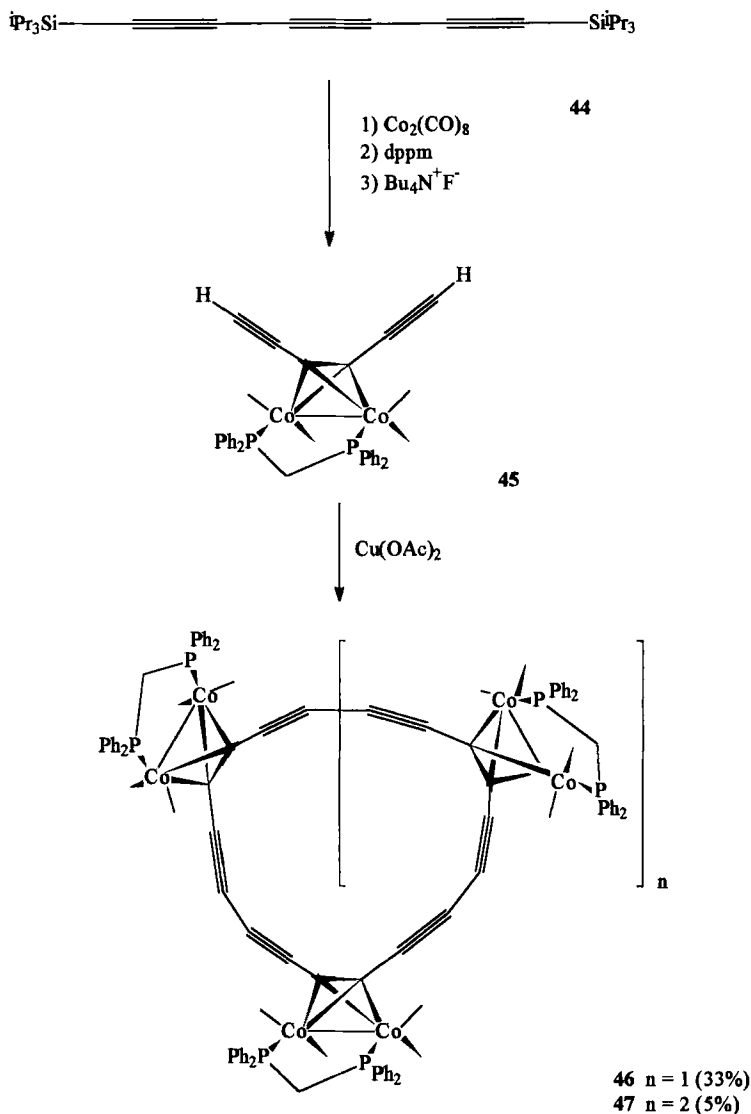


Highly efficient asymmetric intermolecular Pauson-Khand reactions have been developed by using the chiral phosphine ligand (*R*)-(+)-glyphos and *N*-methylmorpholine *N*-oxide as a promoter (see Section II,C).¹⁷⁸

As mentioned in Section II,A, the ready coordination, relative stability, and easy subsequent removal of the hexacarbonyldicobalt unit have resulted

in the use of this group to protect the acetylenic triple bond. The hexacarbonylalkyne–dicobalt complexes are sufficiently inert to allow remote reductions, dehydrations, hydroborations, radical additions, dipolar cycloadditions, and Freidel–Crafts and Wittig reactions.⁷⁴

The relative stability of hexacarbonylalkyne–dicobalt complexes com-



SCHEME 17.

bined with their intense cobalt–carbonyl ν_{CO} vibrations has led to their use as FTIR markers in biological studies.¹⁷⁹ Carbonylmetalloimmunoassay techniques provide a nonradioactive alternative for the assay of hormonal receptor sites.^{180,181}

The structural distortion of alkynes coordinated to hexacarbonyldicobalt units has been exploited in the synthesis of metal complexed *cyclo*[18]carbon and *cyclo*[24]carbon (see Scheme 17).^{182–184} One-pot reaction of the hexatriyne **44** with $[\text{Co}_2(\text{CO})_8]$ followed by dppm and then $[\text{Bu}_4\text{N}]^+\text{F}^-$ affords complex **45**. The dppm imparts the extra stability necessary for the dicobalt unit to withstand treatment with $[\text{Bu}_4\text{N}]^+\text{F}^-$ to remove the $\text{Si}(\text{iPr})_3$ groups. Oxidative coupling under high dilution conditions affords the *cyclo*- C_{18} (**46**) and *cyclo*- C_{24} (**47**) derivatives.

VII

CONCLUSIONS

The study of polynuclear cobalt–alkyne clusters has provided insight into the coordination, protection, and activation of the carbon–carbon triple bond. It is possible to draw analogies between alkynes coordinated to molecular species and those to surfaces.

The chemistry of hexacarbonylalkyne–dicobalt complexes is the most developed of that of the various systems discussed in this review and is finding many applications in organic synthesis. Considerable progress has been made with chiral systems involving mixed-metal cores or asymmetric phosphines, but there are many problems still to be addressed. The detection of radical intermediates has led to coupling reactions applied to the high-yield synthesis of cyclic enediynes. Coupling of several dinuclear radical species offers the possibility of organometallic polymer formation.

Continuing expansion of the chemistry of polynuclear cobalt–alkyne complexes is expected, especially in the areas of reactivity and synthetic applications, in the coming years.

ACKNOWLEDGEMENT

Figures of molecular structures and analyses of molecular geometries were obtained using the Cambridge Structural Database¹⁸⁵ as provided by the EPSRC's Chemical Database Service at Daresburg.¹⁸⁶

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Rhenium and Technetium Oxo Complexes in the Study of Organic Oxidation Mechanisms

KEVIN P. GABLE

*Department of Chemistry
Oregon State University
Corvallis, Oregon 97331*

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I

INTRODUCTION

Oxidation of organic compounds in general and alkenes in particular is an enormous area, and transition-metal-based catalysts have played a pivotal role. Several books have summarized the state of the art.¹ Historically, this has been an area in which empirical development of catalytic oxidation systems has outpaced mechanistic understanding. However, with the recent advent of new synthetic techniques, the number of well-characterized metal oxo compounds has expanded considerably in the past 15 years,² and the prospect of understanding the behavior of the M=O bond in reactions which create C—O bonds has drawn within reach.

The Group 7 metals technetium and rhenium have not been applied to the problem of oxidation chemistry to the level of their Group 6 and Group 8 counterparts. This is understandable in light of their relative scarcity. Technetium is a synthetic element, recovered as a fission by-product from uranium.³ ⁹⁹Tc is radioactive (β^- decay, 0.3 MeV, $\tau_{1/2} = 2.14 \times 10^5$ years) and its use even in the laboratory requires the appropriate safety precautions. Rhenium is not plagued by either issue, yet it is still a relatively rare element, present at only an estimated 0.001 ppm in the Earth's crust. It is

isolated as a by-product from refining molybdenum ore, most commonly as KReO_4 .⁴

Yet the similarity of the chemistries of these two elements with those of Mo, W, Ru, and Os makes them attractive models for probing reaction mechanisms for compounds of metals in the middle of the transition series. Also, as this chemistry has developed it has become clear that there may be unique applications of these two metals, particularly for rhenium. This review will outline the new mechanistic understanding of organic oxidation chemistry that has been generated over the past dozen years by using high-valent metal oxo compounds of technetium and rhenium.

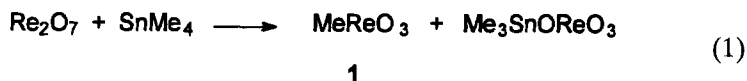
In general, the question of mechanism in this oxidation chemistry centers around several issues. First, what chemical species make up the catalytic cycle? Second, what is the nature of the interaction between the catalytic metal complex(es) and the substrate? Specifically, is there a metal-substrate bond that forms at some point, or are all C—O bond formations occurring remote from the metal? Finally, what is the timing of C—O bond formation relative to other bonding reorganization? Separate but related issues include the sequence of reactions (e.g., hydrolysis, reoxidation) that must occur efficiently to achieve catalytic turnover, and the rates of side reactions such as overoxidation of the product or degradation of the catalyst.

II

METHYL RHENIUM TRIOXIDE (MTO)

A. Preparation, Structure, and Chemical Behavior of MTO

Methyltrioxorhenium(VII) (hereafter referred to as MTO, **1**) was first observed as a by-product created from air oxidation of oxotetramethyl rhenium or trimethyldioxorhenium.⁵ For several years it remained an oddity as an air- and water-stable, high-valent organometallic complex. The compounds from whence it arose were at that time rare examples of stable alkyl metal oxo systems.⁶ However, in 1988 Herrmann *et al.* reported the first of several refined synthetic routes to this compound and began to develop an understanding of its reactivity.⁷ The original deliberate synthesis was a direct alkylation of Re_2O_7 with Me_4Sn :



Preparation of methyltechnetium trioxide **2** by a similar procedure was reported soon after.⁸ This approach has the disadvantage of creating a full

TABLE I
Re—O BOND LENGTHS, O—Re—O BOND ANGLES, AND Re=O INFRARED STRETCHING

	Re=O	O—Re—O	$\nu_{\text{Re=O}}$ (cm ⁻¹)	Ref.
MTO			999, 960	5
MTO–quinuclidine			939, 908	10
MTO–bipy(SO ₃) ⁻ NBu ₄ ⁺			941	13
			918	
			855	
MTO–aniline	1.736; 1.696 1.687; 1.699 1.698; 1.701	105.6; 118.4 105.1; 118.7 116.1; 118.2	927	14
EtReO ₃ –quinuclidine	1.707 1.696 1.703	118.1	922	15

equivalent of the stannyl perrhenate byproduct. In later years, significant improvement was achieved through the use of perfluorinated anhydrides.⁹ These convert both metal centers from Re₂O₇ into highly reactive perfluoroacyl perrhenate, which can then be metalated with Sn(CH₃)₄, or with other alkyl or aryl tin compounds. The failure of the method for making Cp*ReO₃ (Cp* = η -C₅Me₅) was attributed to a mismatch of redox potentials between Cp*SnBu₃ and the acyl perrhenate.

An important practical consideration is the choice of the anhydride; trifluoroacetic anhydride is quite readily available, but the byproduct trimethyltin trifluoroacetate is approximately as volatile as MTO, and the usual purification (sublimation) can be quite difficult. However, use of perfluoroglutaric anhydride results in a relatively nonvolatile tin perfluoroglutarate, allowing for a straightforward isolation of MTO.

MTO is an off-white crystalline solid which is stable to the ambient atmosphere. It is soluble in common organic solvents and in water, although it decomposes in water at high pH to form methane¹⁰ (see later discussion). It is easily sublimed and should be stored in a sealed container. It is reported to have a high photoreactivity in aqueous solutions.¹¹

A substantial portion of the early interest in MTO pertained to its use in alkene metathesis.¹² Of more relevance to oxidation processes, much work has also involved examining Lewis base adducts of this electrophilic, (formally) 14-electron complex. Generally, nitrogen bases coordinate *trans* to the methyl group. Bidentate ligands such as bipyridyl lead to the fac-Me(N[—]N)ReO₃ isomer of the octahedral complex. Table I summarizes some of the structural information from X-ray crystallographic and infrared studies.

B. Catalysis of Alkene Epoxidation

Although the initial report of MeTcO_3 included the observation of its oxidation of tetramethylethylene to form a diolate complex (see Section III), the first report of an organic oxidation mediated by MTO was not published until 1991.¹⁶ This indicated that MTO acted in a catalytic capacity to mediate epoxidation of a wide range of alkenes using H_2O_2 as a stoichiometric oxidant. The viable substrates included simple olefins: terminal, *cis*, *trans*-1,2 disubstituted, trisubstituted, and tetrasubstituted; both π bonds in dienes were usually oxidized; ester, alcohol, aldehydes, and carbonyls all allowed selective oxidation of the alkene without overoxidation. Conditions used were 0.1 to 1.0 mol% MTO (vs alkene) used in a 1.8 M solution of H_2O_2 in *tert*-butanol; temperatures ranged from 0°C to ambient, and times from 0.1 to 24 h. Under the conditions reported, many of the epoxides opened to form the *trans*-vicinal diol. Combined yields of epoxides and diols typically ranged from 60–100% (see Table II).

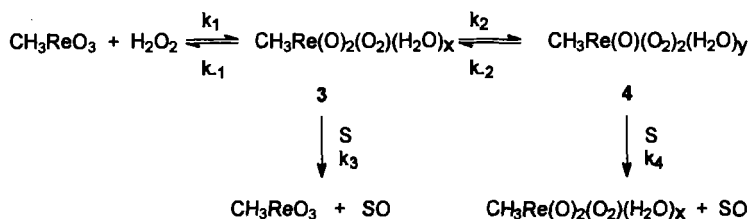
The chemistry of MTO with hydrogen peroxide has been the topic of a long series of papers from both the Herrmann group in Munich and the Espenson group at Iowa State University. Espenson first characterized by UV a pair of new complexes **3** and **4**,¹⁷ which appeared to be kinetically competent in the oxidation of substrates such as thiolatocobalt complexes.¹⁸ These two new complexes were assumed to be the 1:1 and 2:1 H_2O_2 adducts of MTO. The UV spectrum of H_2O_2 /MTO mixtures shows a characteristic peak at around 360 nm. Both new adducts were found to absorb at this wavelength, but a careful analysis of absorption vs stoichiometry and nonlinear least squares fitting allowed determination of both molar absorptivities and equilibrium constants for formation of each species. Kinetic analysis of the rate of formation of each species was consistent with the UV determination of binding constants. The Herrmann group considered an extensive array of rhenium species as potential alternatives to or competitors with these species,¹⁹ but found in all cases that these were either completely inactive or converted to the peroxo complexes under the reaction conditions.

Herrmann proposed a catalytic cycle in the 1991 paper¹⁶ that involved both a mono- H_2O_2 adduct and a bis adduct, and suggested the latter was responsible for epoxidation. However, the Espenson group proposed the kinetic scheme outlined in Scheme 1 to sort out the equilibrium and kinetic behavior of MTO with H_2O_2 ¹⁸; this made no initial assumption about which species was active. At wavelengths above 360 nm, neither MTO nor H_2O_2 has an appreciable UV absorbance, so the Beer's law behavior will be described by $A_{\text{total}}/b = \epsilon_3[\mathbf{3}] + \epsilon_4[\mathbf{4}]$. By solving the appropriate expressions for equilibrium constants K_1 and K_2 , they arrived

TABLE II
TYPICAL YIELDS AND SELECTIVITIES FOR MTO-CATALYZED OXIDATION OF ALKENES^a

Alkene	<i>T</i> (°C)	<i>t</i> (h)	Product	Yield (%, based on reacted alkene)
Propene	−10	12	1,2-Epoxypropane	50
			1,2-Propanediol	50
2-Butene	−10	6	2,3-Butanediol	100
<i>cis</i> -2-Pentene	25	3	<i>cis</i> -2,3-Epoxy pentane	90
			2,3-Pentanediol	10
2,3-Dimethyl-2-butene	25	1	2,3-Dimethyl-2,3-butanediol	75
	−25	16	2,3-Dimethyl-2,3-butanediol	50
			2,3-Dimethyl-2,3-epoxybutane	40
<i>trans</i> -4-Octene	25	2	<i>trans</i> -4,5-Epoxyoctane	95
Cyclohexene	10	5	1,2-Epoxy cyclohexane	90
4-Vinylcyclohexene	15	2	1,2-epoxy-4-vinylcyclohexane	50
			1,2-Dihydroxy-4-vinylcyclohexane	40
1-Methylcyclohexene	25	2	1-Methyl-1,2-cyclohexanediol	70
Methyl oleate	25	24	Methyl 9,10-dihydroxyoctadecanoate	92
Allyl alcohol	25	10	2,3-Epoxy-1-propanol	90
Crotonaldehyde	25	24	2,3-Epoxybutanal	60
1,4-Naphthoquinone	70	18	2,3-Epoxy-1,4-naphthoquinone	64
<i>cis</i> -1,4-Dichloro-2-butene	25	48	1,4-Dichloro-2,3-epoxybutane	73

^a Adapted with permission from Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 1638–1640; also adapted from Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *Alkylrhenium Oxides as Homogeneous Epoxidation Catalysts: Activity, Selectivity, Stability, Deactivation*; *J. Mol. Catal.* **1994**, 86, 243–266 (copyright 1994) with kind permission of Elsevier Science—NL, Sara Burgerhertstraat 25, 1055 KV Amsterdam, The Netherlands.



SCHEME 1.

at the following expression for absorption as a function of total (initial) MTO concentration $[\text{MTO}]_{\text{T}}$:¹⁷

$$\epsilon = \frac{A}{[\text{MTO}]_{\text{T}}} = \frac{\epsilon_3 K_1 [\text{H}_2\text{O}_2] + \epsilon_4 K_1 K_2 [\text{H}_2\text{O}_2]^2}{1 + K_1 [\text{H}_2\text{O}_2] + K_1 K_2 [\text{H}_2\text{O}_2]^2} \quad (2)$$

(The two complexes were subsequently shown to have similar but distinct UV spectra: **3** has $\lambda_{\text{max}} = 310$ nm, and **4** has $\lambda_{\text{max}} = 364$ nm.²⁰) By varying the initial MTO concentration and perchloric acid concentration, and by examining the system at several wavelengths, sufficient data were generated to establish a good least-squares fit to this expression. With a knowledge of the molar absorptivities and formation constants for each rhenium species, it became a routine matter to choose conditions under which one or the other peroxide complex predominated. Not surprisingly, at low concentrations of H_2O_2 , compound **3** predominates, whereas in solutions where $[\text{H}_2\text{O}_2] > 0.50$ M and $[\text{MTO}]_{\text{T}} = (3.2\text{--}8.0) \times 10^{-4}$ M, **4** predominates. The directly measured molar absorptivities seen for the latter coincide nicely with those obtained from the least-squares fit to Eq. (2).

The confirmation of structure for one of these required X-ray crystallography of a diglyme complex (Fig. 1), reported by Herrmann *et al.*²⁰ This

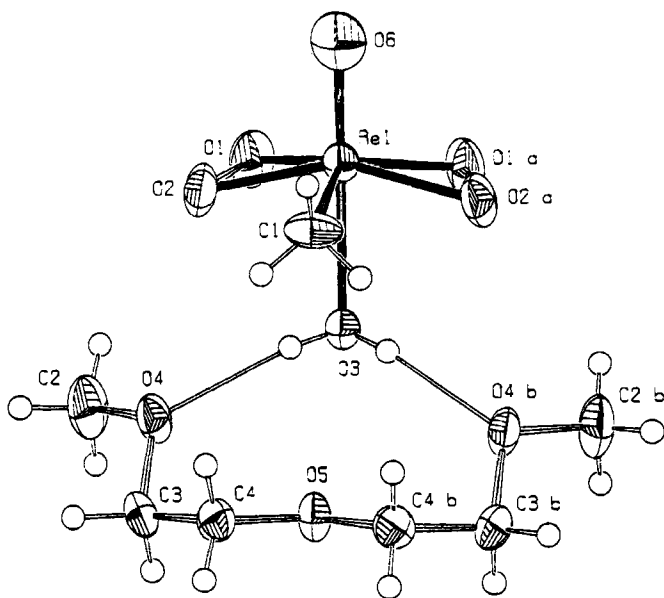


FIG. 1. Solid-state structure of the diglyme complex of **4**. [Reproduced with permission from Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1157–1160.]

TABLE III
RATE AND EQUILIBRIUM CONSTANTS FOR FORMATION OF **3** AND **4** FROM H_2O_2 AND MTO^a

Conditions	k_1	k_{-1}	k_2	k_{-2}	K_1	K_2	Ref.
25°C, 0.1 M HClO_4 , [H_2O_2] = 0.32 mM	77	9.0					18
25°C, 0.02–0.2 M HClO_4	80	10	5.2	0.04	7.7	145	17
25°C, H_2O , pH = 0.0	42.2	2.62	5.2	0.039	16.1	132	21
25°C, 1:1 MeCN/ H_2O , pH = 1.0	30	3.2	1.05	0.008	10.8	136	23
25°C, 1:1 MeCN/ H_2O , 0.10 M HClO_4	32.5	3.0			13	136	27
25°C, MeOH/ H_2O	1150	4.4	308	.38	261	814	22
25°C, THF, 50 mM 30% H_2O_2	0.074		6.8×10^{-3}				34

^a Units: k_1, k_2 : liter $\text{mol}^{-1} \text{s}^{-1}$; k_{-1}, k_{-2} : s^{-1} ; K_1, K_2 : liter mol^{-1} .

bisperoxide compound might best be considered pentagonal bipyramidal, with two η^2 -peroxide ligands bound in an equatorial plane with the methyl group. The remaining terminal oxo ligand and a water ligand are bound axially, with the water hydrogen bonded through each hydrogen to a molecule of diglyme. Once this bis- η^2 peroxide was characterized, it became clear that the other relevant species was the mono- η^2 peroxodioxo complex. Several of the subsequent papers from the Espenson group further established the behavior of MTO and H_2O_2 under different reaction conditions. Table III shows results reported under several conditions.

The Herrmann group originally claimed (through 1993^{12,13}) little or no oxygen atom transfer reactivity for the monoperoxide adduct **3**. However, substantial work by Espenson and co-workers capitalized on their knowledge of the equilibria to independently characterize the reactivity of both **3** and **4**; knowing the forward and reverse rates for interconversion of **1**, **3**, and **4** allows one to rule out the possibility that all reactivity arises from a single species.

Evaluation of mechanistic rate constants k_3 and k_4 from k_{obs} is rather complex; the full derivation is described in Ref. 23. The full rate expression for formation of product (SO) is given by Eq. (3)^{18, 23}:

$$\frac{d[\text{SO}]}{dt} = \frac{k_1 k_3 [\text{Re}]\text{T}[\text{H}_2\text{O}_2][\text{S}] + \frac{k_1 k_2 k_4 [\text{Re}]\text{T}[\text{S}][\text{H}_2\text{O}_2]^2}{k_4 [\text{S}] + k_{-2}}}{k_{-1} + k_3 [\text{S}] + k_1 [\text{H}_2\text{O}_2] + \frac{k_1 k_2 [\text{H}_2\text{O}_2]^2}{k_4 [\text{S}] + k_{-2}}} \quad (3)$$

This can be simplified; under conditions where $[\text{3}] \ll [\text{4}]$, terms in k_3 approach zero, as do those in k_4 if $[\text{3}] \gg [\text{4}]$. It is also necessary to account for any uncatalyzed oxidation of substrate by $[\text{H}_2\text{O}_2]$ that is competitive under the conditions; normally, this is shown to be negligible. It is, of

TABLE IV
REACTION RATE CONSTANTS FOR MONOPEROXIDE **3** AND BISPEROXIDE **4** REACTING WITH
DIFFERENT SUBSTRATES

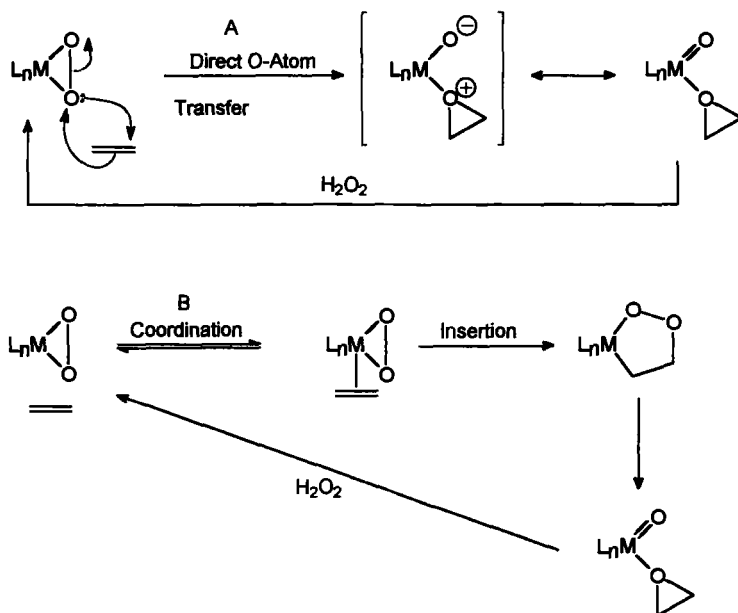
Substrate	Conditions	k_3	k_4	Ref.
(en) ₂ Co(SCH ₂ CH ₂ NH ₂) ⁺	25°C, 0.10 M HClO ₄	4.2×10^{-5}		18
PhSMe	25°C, pH 1, 1:1 MeCN/H ₂ O	2.65×10^3	9.65×10^2	23
PhCH ₂ SMe	"	5.4×10^3		23
PhSPh	"	1.18×10^2	32	23
PPh ₃	25°C, 0.1 M HClO ₄ , 1:1 MeCN/H ₂ O	7.3×10^5	2.1×10^6	27
Ph ₃ As	"	3.7×10^5		27
Ph ₃ Sb	"	5.3×10^5		27
PhNMe ₂	MeOH, 25°C	18.4	0.0114	22
Styrene	25°C, 0.1 M HClO ₄ , 1:1 MeCN/H ₂ O	0.11	"	29
PhC(Me)=CH ₂	"		0.47	29
PhCH=CHMe (<i>cis</i>)	"	0.74	0.28	29
PhCH=CHMe (<i>trans</i>)	"	0.51	0.22	29
PhCH=CMe ₂	"	1.00	0.70	29
1-Methylcyclohexene	"		4.20	32
Methylenecyclohexane	"		0.97	32
Cyclohexene	"		1.06	32
2-Methyl-1-pentene	"		0.55	32
2-Methyl-2-pentene	"		3.92	32
2,3-Dimethyl-2-butene	"		8.93	32
Norbornene	"		1.88	32
Cl ⁻	25°C, 1.0 M HClO ₄	0.059	0.124	21

course, possible to perform nonlinear least-squares analysis to extract the individual rate constants, but more reliable values result from controlling conditions to favor one or the other oxidant. Also, to confirm the validity of Eq. (3) absorbance/time plots can be fitted to it nicely when oxidation of aniline is followed spectrophotometrically at 300 nm.²²

The two peroxo complexes possess remarkably similar reactivities toward most substrates (see Table IV). In all cases the peroxo complexes oxidize the substrate more rapidly than does H₂O₂ alone.

C. Mechanisms for O-Atom Transfer

The assignment of the η^2 -peroxide structure to these reactive intermediates immediately raised several issues. One could surmise that the behavior would be similar to that of the so-called MoOPH reagents, which are also efficient alkene oxidants. Careful labeling studies have shown that the latter transferred oxygen to substrates from the η^2 -peroxide and not from the



SCHEME 2.

terminal oxo ligand. A similar labeling experiment for the rhenium system confirmed that peroxide was the O atom source.²³

Yet even with this process there are two classes of possible mechanism (Scheme 2). One (A) is a direct O-atom transfer.²⁴ This might be viewed as a "nucleophilic displacement" of the electrons in the O—O bond; the oxidized substrate then becomes a weak ligand that is readily displaced from the metal. However, when proposed it has generally been viewed as a concerted atom transfer reaction without the degree of zwitterionic character Fig. 3 implies.^{21,27,29} Cyclocondensation of H_2O_2 with the resulting $\text{M}=\text{O}$ unit regenerates the η^2 -peroxide to continue the catalytic cycle. This at first glance would appear to be the most likely mechanism for oxidation of sulfides, R_3E ($\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}$) and halide.

A second mechanism (B) which may become important for alkenes involves a net insertion into one of the $\text{M}-\text{O}$ single bonds, as proposed by Mimoun.²⁵ The cyclic peroxo structure that then forms would have to undergo a fairly deep-seated rearrangement, but one can imagine that ionic or radical paths might lead as well to the same type of end product as provided by the direct atom transfer. This mechanism posits a more direct role for the metal, requiring as it does substrate binding prior to insertion. However, the d -to- π^* back-bonding which is normally important in metal-

alkene complexes is not possible for d^0 metals, and without this interaction it is debatable how strong the alkene-metal interaction will be²⁶ and whether it is strong enough to induce this type of mechanism.

An initial argument in favor of the direct atom transfer mechanism came from the investigation of triarylphosphine oxidation.²⁷ The authors cite the earlier observation that **4** in solution has a tightly bound and nonexchanging (by ^{17}O NMR) water molecule.²⁰ (This was later shown by ^1H NMR to be inaccurate, but additional arguments later support the general conclusions presented here.³⁴) Therefore, it was unlikely that **4** would exchange ER_3 for H_2O , a necessary process for this complex if the stepwise process operates. Further, given the similar kinetic behavior of **3** and **4**, it seemed unlikely that the two species oxidize substrate via substantially different mechanisms (though this cannot be rigorously excluded). Excess $\text{O}=\text{ER}_3$ should also compete for a coordination site with substrate, but added product has no perceptible effect on the reaction rate. Also, steric influences were seen to be negligible, arguing against substrate coordination to rhenium. Tri-(*o*-tolyl)phosphine and tri-(*p*-tolyl)phosphine have similar electronic behaviors, but markedly different cone angles (194° vs 145°).²⁸ There is less than a factor of 5 between the rates of oxidation of the two by **3**: $\text{P}(\textit{o}\text{-tolyl})_3$: 1.9×10^5 liter $\text{mol}^{-1}\text{s}^{-1}$; $\text{P}(\textit{p}\text{-tolyl})_3$: 9.4×10^5 . Further, a linear Hammett relationship for the oxidation of substituted triarylphosphines was observed with $\rho = -0.63$. This suggests the mechanism is remaining consistent for each substrate, and that the degree of positive charge buildup at phosphorus is fairly small at the transition state.

Similar methodology was used in the investigation of styrene oxidation by **3** and **4**.²⁹ Although many substrates were analyzed for both rate constants, k_4 (reaction of **4**) received heavier focus. Here again, a linear Hammett plot was obtained ($\rho = -0.93$ with σ^+), and other electron-donating methyl substituents accelerated the reaction as well. The authors pointed out the similarity between the behavior of **4** and that of dimethyldioxirane³⁰ ($\rho = -0.90$) and peracetic acid³¹ ($\rho = -1.3$). Steric effects were also small (*cis* vs *trans* β -methylstyrene, Table IV). Activation parameters were measured for k_4 in the oxidation of 4-methoxystyrene; between 3.3 and 37.5°C , $\Delta H^\ddagger = 42.8$ kJ/mol (10.2 kcal/mol); $\Delta S^\ddagger = -106$ J $\text{mol}^{-1}\text{s}^{-1}$ (-25.3 cal $\text{mol}^{-1}\text{K}^{-1}$). These indicate a bimolecular rate-determining step with a significant bond-cleavage component, though significant C—O bond formation was inferred. The data *in toto* were interpreted as being entirely consistent with a concerted O-atom transfer from peroxide to alkene, and less consistent with the stepwise formation of an intermediate metallacycle.

A subsequent series of investigations of aliphatic alkene oxidation similarly argued for a concerted transfer of oxygen from peroxide to alkene.³² Again, the general order of reactivity depended on the electron-donating

properties of the substituents: tetrasubstituted > trisubstituted > disubstituted (*cis* \approx *trans*) > monosubstituted. Electron-withdrawing groups (CO_2R , CN) significantly retarded the reaction. The comparison of methanol to 1:1 aqueous MeCN (an increase in polarity and binding ability of the solvent) accelerates the reaction. Here again there is a close parallel between trends seen for the reactivity of **4** and the reactivity of dimethyldioxirane. The authors further explored the ramifications of the concerted oxygen transfer by considering two slightly different transition state structures (Fig. 2). The first has a planar interaction of atoms with the oxygen undergoing transfer, whereas the second has tetrahedral oxygen. The former might be expected to show somewhat more differentiation between *cis* and *trans* disubstituted alkenes because of a steric clash with methyl and coordinated water ligands. The rate ratio of 1.3 (*c/t*) for β -methylstyrene and 2.5 for 3-hexen-1-ol might argue for the spiro arrangement.

The principle of generating a rhenium η^2 -peroxide has recently been used to demonstrate that the methyl ligand is not a necessary component of this process, though it does impart several practical advantages.³³ Herrmann and co-workers isolated a dinuclear rhenium(VII) peroxide $\text{H}_4\text{Re}_2\text{O}_{13}$ **5** and characterized it (as a diglyme adduct) by single-crystal X-ray diffraction. The structure at rhenium is similar to **4**, with the exception that the methyl group is replaced by an $\text{Re}-\text{O}-\text{Re}$ link. (Fig. 3) Like **4**, **5** also efficiently oxidizes alkenes (among other substrates). However, it suffers extreme water sensitivity, decomposing irreversibly to perrhenic acid in organic solvents containing as little as 12 ppm H_2O .

The $\text{MTO}/\text{H}_2\text{O}_2$ adducts **3** and **4**, on the other hand, are stable in acidic aqueous solution. They do decompose slowly; detailed investigation has

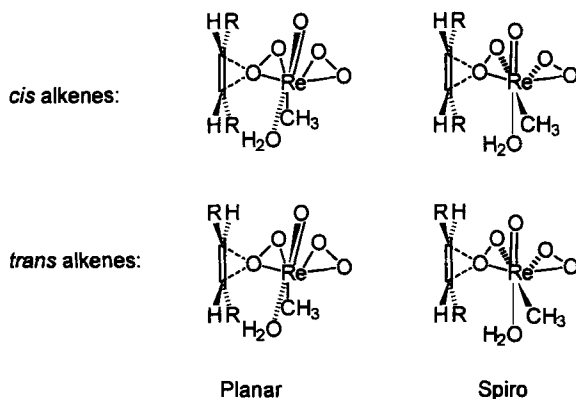


FIG. 2. Comparison of planar and spiro transition state geometries for oxidation of *cis*- and *trans*-alkenes.

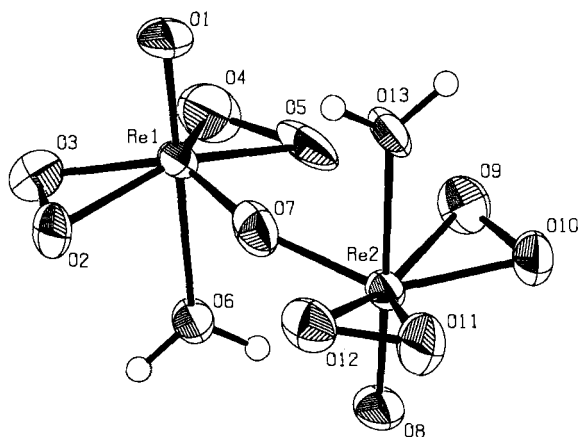
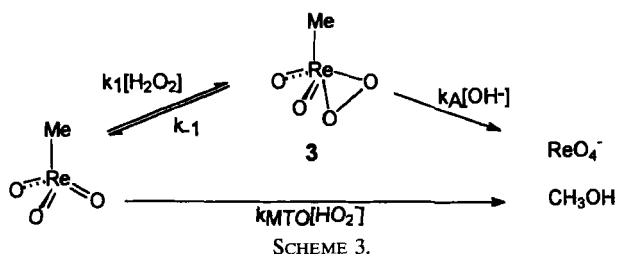


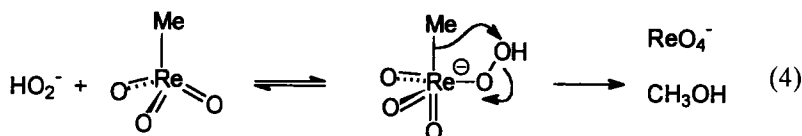
FIG. 3. Solid-state structure of $\text{H}_4\text{Re}_2\text{O}_{13}$. [Reproduced with permission from Herrmann, W. A.; Correia, J. D. G.; Kühn, F. E.; Artus, G. R. J.; Romão, C. C. *Chem. Eur. J.* **1996**, 2, 168–173.]

been reported.³⁴ Variable-temperature NMR spectra show that for **4**, water is coordinated to the rhenium and exchanges on the NMR time scale, in contradiction of an earlier report.²⁰ Complex **3**, on the other hand, shows no identifiable signal for coordinated water above -55°C , so either no water is coordinated or its exchange is much more rapid. In nonaqueous solvents (i.e., mixtures of solvent plus 30% aqueous H_2O_2 , partially dried over MgSO_4), **4** is stable, particularly in the presence of excess H_2O_2 . Slow base-catalyzed decomposition to MTO and O_2 is observed for **4**. If $[\text{H}_2\text{O}_2] \ll [\text{Re}]_{\text{T}}$ (i.e., **3** is the major species present), then decomposition to methanol (detected by NMR) and perrhenate (detected by UV) is observed. Aqueous solutions decompose readily in the absence of added acid, though at $\text{pH} = 1.0$ the process is slow.

The decomposition of each species represents a mechanistically interesting process, and the further kinetic analysis reported in ref. 34 sheds light on these. However, the decomposition of **3** is complicated by the presence of two kinetically indistinguishable pathways, shown in Scheme 3.



One of these (k_A) is attack by hydroxide on **3**. This might entail nucleophilic attack by hydroxide on the methyl group, with subsequent or concomitant fragmentation of the η^2 -peroxide to form terminal oxos.³⁵ However, the system will also have some free H_2O_2 , which would be deprotonated by the base ($\text{p}K_a\{\text{H}_2\text{O}_2\} = 11.62$, vs 15.74 for H_2O).³⁶ The hydroperoxide anion could then attack free MTO:



An attempt to distinguish the two by ^{18}O labeling was frustrated by exchange in the perrhenate product. However, the authors favored the latter mechanism, based on the observation that the observed rate constants suggested that k_A or k_{MTO} had to be near the diffusion-controlled limit, coupled with the known higher nucleophilicity of the hydroperoxide vs hydroxide anions.³⁷ The formation of the new C—O bond in this case is thus reminiscent of the oxidation of alkylboranes with hydrogen peroxide.³⁸

Equally intriguing is the decomposition of **4**. Dioxygen was detected using an oxygen electrode; quantitative GC analysis showed less than 2.2% production of methane, based on starting rhenium. The rate of O_2 evolution varied inversely with $[\text{H}_2\text{O}_2]$, whereas the final yield of O_2 varied linearly with peroxide. Thus the stoichiometry in Eq. (5) was arrived at:

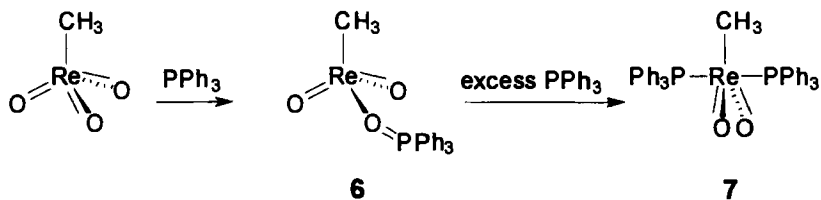


Since MTO is reconverted to **4** under the conditions, this amounts to a disproportionation of H_2O_2 that is catalytic in rhenium.

Some insight into the divergence in the behaviors of the two peroxides was gained by noting the stability of the products formed in each instance, as opposed to the instability of putative products formed by imposing one decomposition path on the other peroxide. Specifically, if **3** were to lose O_2 , the product would be MeReO_2 , a highly reactive Re(V) compound.³⁹ Likewise, **4** could in principle be attacked by hydroperoxide, but the product of methanol expulsion would be $\text{Re}(\text{O})_3(\text{O}_2)^-$, a species that has never been detected in perrhenate/ H_2O_2 mixtures.

A separate line of investigation has explored oxygen atom transfer to

renium. The alkylrhenium trioxides (including Cp^*ReO_3) can be reduced by phosphines to species that can formally be described as RReO_2 complexes. Thus, MTO reacts with triphenylphosphine to yield **6**, a reduced rhenium with a coordinated $\text{Ph}_3\text{P}=\text{O}$.⁴⁰ The phosphine oxide can be displaced by excess phosphine to produce **7**⁴¹:



(6)

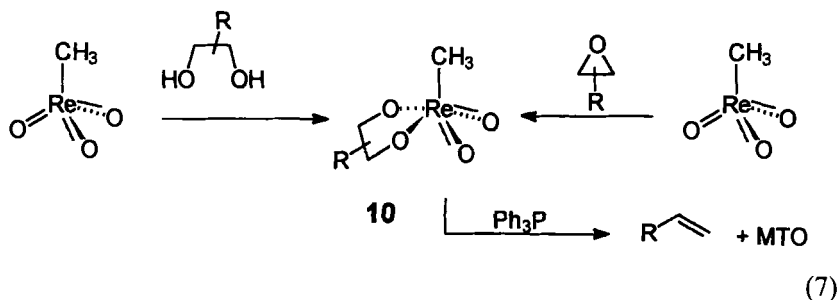
Adduct **7** reacts with O_2 to generate phosphine oxide, and the process can be made catalytic in rhenium.⁴²

This reactivity with O_2 is reminiscent of the behavior of the Cp^* analog. Reduction of Cp^*ReO_3 **8** with PPh_3 yields dimeric $(\text{CpReO})_2(\mu\text{-O})_2$ **9**.⁴³ This $\text{Re}(\text{V})$ complex reacts rapidly with O_2 to cleave the $\text{O}-\text{O}$ bond and regenerate Cp^*ReO_3 in high yield.

One factor that appears to drive this chemistry is the strength of the $\text{Re}=\text{O}$ bond in MTO. It can be argued that this is also a factor in the epoxidation chemistry of **3** and **4**, because both regenerate the $\text{Re}=\text{O}$ unit upon O-atom transfer. In the case of reduced $\text{Re}(\text{V})$ systems, the atom transfer can be turned around to effect a deoxygenation of epoxides in two instances. Gable and co-workers observed that $(\text{Cp}^*\text{ReO})_2(\mu\text{-O})_2$ reacted with epoxides to generate Cp^*ReO_3 and the corresponding alkene.⁴⁴ The fragmentation of the dimer was observed by variable-temperature NMR, and accordingly the deoxygenation was presumed to go through this intermediate. The reaction rate law was half-order in dimer, consistent with this supposition. However, it was not possible to distinguish two possible mechanisms. A concerted O-atom transfer (probably via an intermediate O-coordinated epoxide) would be similar to the epoxidations via **3** and **4** shown earlier. This mechanism has been proposed for epoxide deoxygenations by early transition metal complexes.⁴⁵ However, neither the rate nor the dimer/monomer equilibrium showed any appreciable solvent effect (THF vs benzene). Such an effect might be expected for the concerted process, given presumed competition for weak binding to the metal between THF and the epoxide. An alternative would be for the d^2 metal center to effect an oxidative addition,⁴⁶ followed by fragmentation of the alkene from the

intermediate metallaoxetane (see Section III). Radical intermediates were excluded on the basis of the observed stereospecificity.

A related process is seen for MTO systems. Espenson and co-workers observed that MTO induced a ring expansion of epoxides⁴⁷; condensation of diol with MTO (a common reaction for rhenium oxides⁴⁸) gives a dioxodiolate complex **10**:



Diolate **10** was apparently not formed by hydrolysis of the epoxide, but was in fact a result of rearrangement that occurs within the coordination sphere of the rhenium. In the presence of phosphine, oxo transfer to Ph_3P presumably creates a Re(V) diolate that rapidly extrudes alkene. The mechanism for the latter was not discussed.

D. Miscellaneous Oxidations Using MTO/ H_2O_2

The MTO/ H_2O_2 system has been used to oxidize several other classes of substrates. Internal alkynes may be oxidized to α -diketones and/or carboxylic acids, whereas terminal alkynes are oxidized to mixtures of carboxylic acids, -ketoacids, and (in alcoholic solvents) esters.⁴⁹ These conversions are proposed to proceed through an oxirene intermediate by analogy to the alkene epoxidations discussed earlier.

A second class of oxidation in which these systems have been applied is conversion of electron-rich arenes to quinones.⁵⁰ Oxidation of 2-methylnaphthalene showed a significant selectivity for formation of 2-methylnaphthoquinone over the 6-methyl isomer. This was later proposed³³ to proceed via epoxidation of the electron-rich arene ring, followed by ring opening and further oxidation of the hydroquinone.

A related piece of work by Russian workers showed that anisole was oxidized to a mixture of *o*- and *p*-methoxyphenol by MTO/ H_2O_2 in MeCN.⁵¹ Oxidation of benzene to phenol was also observed, though this process was far slower. As with the hydroquinone oxidations, this likewise can be

rationalized on the basis of an initial epoxidation, followed by ring opening to the phenol. Preference was for placement of the new C—O bond at the *ortho* position (2:1), although this can be perturbed somewhat with addition of water or methyl *t*-butyl ether. A kinetic analysis was performed; the rate law is reported to be first-order in substrate and in rhenium, though the expected dependence on $[H_2O_2]$ was not reported.

The MTO/ H_2O_2 system has been observed to insert oxygen into aliphatic C—H bonds.⁵² The selectivity parallels susceptibility to radical-induced C—H cleavage: $R_2CH-OR' > R_3CH > R_2CH_2$; methyl oxidation was not observed. However, radicals are probably not involved, as retention of stereochemistry is observed for both *cis*- and *trans* decalin and for *cis*- and *trans*-1,2-dimethylcyclohexane. Yields of oxidized products varied greatly and may be dependent on steric effects: *cis*-decalin gave 90% conversion to 9-hydroxy-*cis*-decalin, whereas the *trans* isomer gave only 20% yield (measured by GC vs internal standard). Adamantane gave an 88% yield of 1-adamantanol. Typical conditions used *tert*-butanol as solvent, temperatures of 40–60°C, and reaction times of 24–72 h.

A final oxidation type that has been observed is the catalysis of Baeyer–Villiger-type oxidations of cyclic ketones to lactones.⁵³ Understandably, the strained cyclobutanone is the best substrate, giving 80% conversion after 24 h at 25°C (*tert*-butanol solvent). Larger ring ketones proceed more slowly, although selectivity remains high. Elevated temperatures increase the rate without sacrificing selectivity: cyclopentanone is converted to the lactone in 72% yield after 1 h at 70°C in THF. Complex **4** was presumed to be the active species.

Little related work on the technetium analog has been completed. Much of the synthetic work with high-valent Tc has centered on imido complexes,⁵⁴ or on complexes for use in radiopharmaceuticals.⁵⁵ Methyl technetium trioxide has been prepared.⁸ This species is thermodynamically a powerful enough oxidant to cycloadd to alkenes; cyclohexene gave (after hydrolysis) *cis*-1,2-cyclohexanediol. No chemistry with H_2O_2 has been reported; it is expected to behave in a similar manner to MTO, unless the change in the metal–oxo bond strength perturbs the overall thermodynamics.

III

BISHYDROXYLATION OF ALKENES

A. History of the Mechanistic Problem

For much of this century, osmium tetroxide and potassium permanganate were alone in their ability to bishydroxylate alkenes. Such reactions are as

attractive as epoxidations: They create two new functional sites in the molecule. Likewise, it is possible for the reaction to create new stereocenters with total control of the relative configuration, and recent advances have revealed methods for absolute control of stereochemistry.⁵⁶ This chemistry has been extensively reviewed.⁵⁷ However, the mechanism remains an area of active discussion.

Since Criegee's pioneering work in the late 1930s, the accepted mechanism for hydroxylation has been a concerted cycloaddition of alkene to the $\text{O}=\text{Os}=\text{O}$ system.⁵⁸ The development of the theory of pericyclic reactions in the 1960s and 1970s helped cement this proposal firmly in the minds of many workers.⁵⁹ However, subsequent work has found few (if any) documented organometallic examples that followed the Woodward-Hoffmann rules.

In 1977, Sharpless proposed the intermediacy of a four-membered metal-lacycle in the oxidation of cyclododecene by CrO_2Cl_2 .⁶⁰ This was an attempt to explain a minor but primary product, in which an oxygen and a chlorine were added in a *syn* fashion to one face of the β -bond. Later, this type of intermediate was incorporated into a new mechanism for osmylation,⁶¹ in which an initial $[2 + 2]$ cycloaddition led to an osmaoxetane which in a second step underwent ring expansion to form the observed metal diolate product. At the time, the $[2 + 2]$ process was viewed as a violation of orbital symmetry rules, and it was not until the extensive work in the 1970s and 1980s on cycloadditions to metal carbenes that a theoretical basis for such a process allowed its broader acceptance.

The following years saw many attempts either to find support for this mechanism or to discredit it. One claim that the key intermediate had been observed⁶² was immediately shown to be in error.⁶³ For many organic chemists, the symmetry considerations of the initial net $[2 + 2]$ cycloaddition were sufficient to discard it in favor of the (claimed) symmetry-allowed $[3 + 2]$ process, which itself appeared to be similar to the concerted cycloaddition of (among other reagents) ozone to an alkene. However, as the chemistry of $\text{M}=\text{E}$ ($\text{E} = \text{CR}_2, \text{NR}$) systems developed in the 1980s, it became clear that formation of four-membered rings was actually a common mode of reaction. Further, as synthetic routes were developed to make metallaoxetanes, it was found in several instances⁶⁴ that they decomposed by retro- $[2 + 2]$ reactions, most often to form alkenes plus metal oxo systems. This is the microscopic reverse of Sharpless's first step in the stepwise osmylation mechanism.

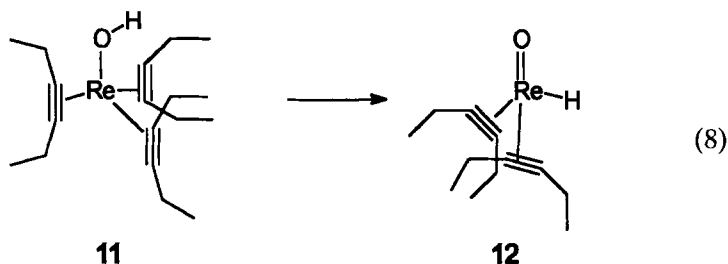
However, the stepwise mechanism proposed a second step requiring the migration of an alkyl group to an oxo ligand. This has very little precedent. Prior to 1990, there were but a handful of possible examples, and in none of these were the oxo alkyl and the subsequent alkoxide directly observed

(see later discussion). It appeared that osmylation was either a unique example of a metallapericyclic process, or a stepwise process for which one step was largely without precedent. In recent years work on Tc and Re complexes has provided insight into the viability of the latter possibility.

B. Migration to an Oxo Ligand

Specific examples of alkyl migration between a metal and an oxo ligand have been rare. The first claim for such a process was the isolation of phenol from treatment of VOCl_3 with Ph_2Hg .⁶⁵ The presumed intermediate, phenyl vanadate, was not isolated. In the intervening years, the increasing number of stable alkyl metal-oxo complexes² (MTO being a quintessential example) suggested the presence of a kinetic barrier to this transformation. The absence of much thermodynamic data also made it difficult to predict whether these new complexes owed their stability to such a kinetic barrier, or whether the alkoxide was inherently less stable than the oxo in any particular case. The latter is almost certainly true for early transition metals, and by the late 1980s, a small number of examples of the reverse process had been observed, particularly for tantalum.⁶⁶

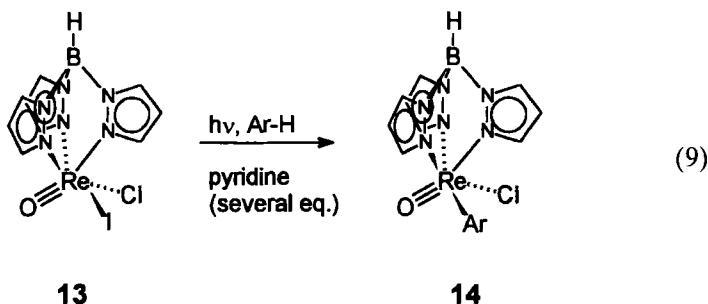
One important example of this class of rearrangement was reported for a rhenium complex in 1993⁶⁷ and, in retrospect, took advantage of the lower barrier of hydrogen migrations as compared to alkyl migrations. Mayer and co-workers prepared the tris-acetylene hydroxide complex **11**, as well as the oxo hydride **12**. Upon standing at room temperature for 5 days in benzene solution, the hydroxide spontaneously forms the oxo hydride with loss of one equivalent of acetylene, as shown in Eq. (8).



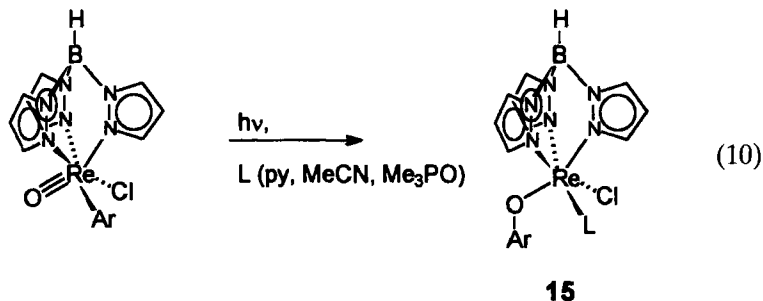
This was cleanly first-order, $k_{\text{obs}} = 5.6 \times 10^{-6} \text{ s}^{-1}$ at 294 K; an Eyring plot between 294 and 327 K gave activation parameters $\Delta H^\ddagger = 17 \text{ kcal/mol}$ and $\Delta S^\ddagger = -25 \text{ cal/(mol}\cdot\text{K)}$. A primary kinetic isotope effect of approximately 5 was seen for the deuterioxide at 294 K. No rate inhibition was seen in the presence of added alkyne, leading to the conclusion that preequilibrium loss of alkyne did not occur and that the rate-determining step was in

fact rearrangement of **11**. Exchange of external alkyne into the starting hydroxide was shown to be slower than the rearrangement. The possibility of deprotonation/reprotonation as a reaction path was considered; the hydroxide can be deprotonated to give an oxo anion, and reprotonation does generate **12**. However, in contrast to the solution behavior of the hydroxide, this two-step reaction is not clean. Finally, the oxo anion rapidly abstracts iodine from *p*-iodotoluene, and this reagent has no effect on the rearrangement of **11**.

Analogous alkoxy and aryloxyrhenium complexes do not show the same reactivity. However, Brown and Mayer discovered soon thereafter that a different rhenium complex could mediate C—O bond formation.⁶⁸ Photolysis of the Re(V) complex **13** led to C—H activation and formation of a phenyl rhenium oxo, **14**. Yields were improved from 30–40% to 90% upon addition of pyridine to the photolysis mixture. The role of pyridine was unclear, because other tertiary amines provided no such improvement in yield. Substituted benzenes showed a preference for *para* activation over *meta*; fluorobenzene also gave a significant amount of *ortho* activation.



This aryl rhenium oxo complex was thermally stable (160°C for 30 days). However, UV photolysis in the presence of pyridine slowly caused conversion of this compound to the rhenium(III) phenoxide **15**. Despite the slow rate (80% conversion in 10 days), the selectivity was high (85%). Evidence for the coordinatively unsaturated intermediate TpReClOAr (**16**, Tp = hydrido-tris-pyrazolylborate) was seen in the O-atom transfer from DMSO to form the rhenium(V) phenoxide TpRe(O)ClOAr, **17**. Other ligands (MeCN, Me₃PO) may also be used to trap the Re(III) complex. A double-label crossover experiment showed less than 15% crossover, confirming the intramolecular nature of the migration, and substituted phenyl groups undergo migration without rearrangement. Neither CD₃CN ($k_{\text{trap}} = 10^5 \text{ M}^{-1} \text{ s}^{-1}$) nor PhSH ($k_{\text{trap}} = 10^9 \text{ M}^{-1} \text{ s}^{-1}$) led to trapping of the phenyl radical.

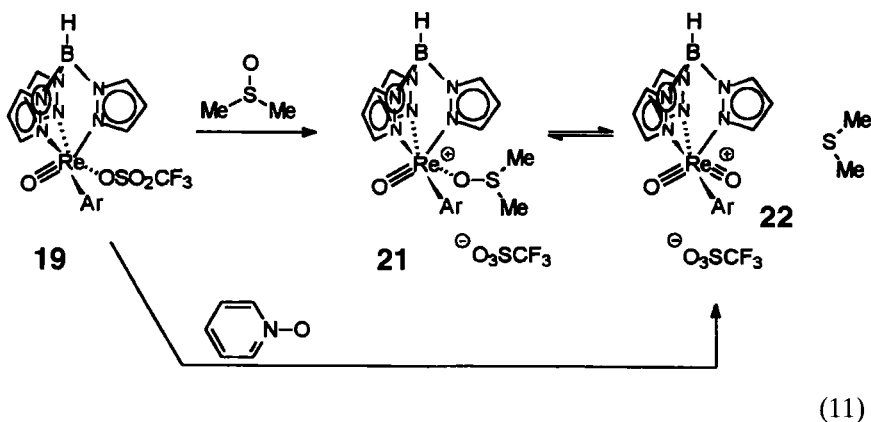


Alkyl analogs of **14** also experience migration of the organic group to oxygen. The ethyl compound produces the ethoxide **16**, although the yield is lower and accompanied by significant amounts of ethane and ethene. Addition of O_2 or PhSH suppresses formation of the ethoxide. These data strongly suggest that the alkyl migrations proceed via a radical pathway involving C—Re homolysis. It is conceivable that the phenyl migration is also a radical process occurring within a cage, though one would expect the more stable phenyl radical to show a higher propensity for cage escape. The authors suggest it seems more likely that participation of the aryl π system circumvents the homolytic cleavage of the C—Re bond in these compounds. One clear conclusion is that there is a significant barrier to the thermal migration; based on rate of slow thermal decomposition of the phenoxide (several days at 120°C ; no **14** is formed), $\Delta G^\ddagger > 32$ kcal/mol.

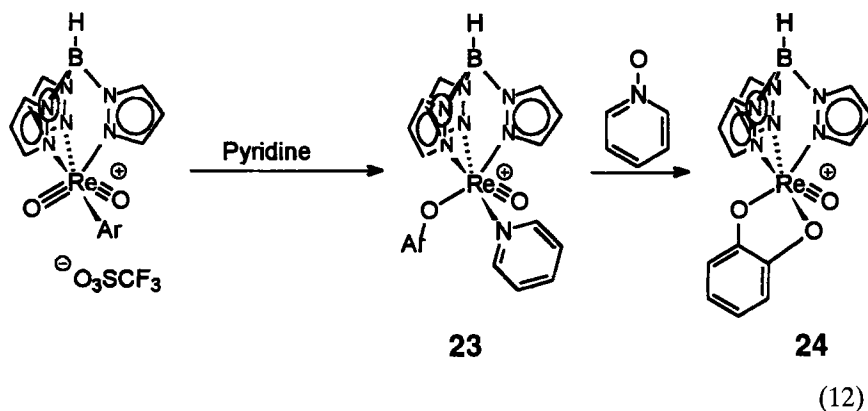
Clues to the nature of the barrier to alkyl-to-oxo migration were seen in work by Brown and Mayer.⁶⁹ Although the Re(V) alkyl oxo complexes discussed earlier are inert to thermal rearrangement, it is possible to generate a Re(VII) alkyl dioxo complex at low temperatures, and to observe its rearrangement to a Re(V) alkoxide. Aryl complexes $\text{TpRe}(\text{O})\text{Ar}_2$ **17** (prepared by alkylation of the corresponding dihalide) react selectively with I_2 at short reaction times to form $\text{TpRe}(\text{O})\text{ArI}$ (**18**). Reaction with AgOTf yields the triflate **19** as a covalent complex, based on ^{19}F NMR and IR behavior. (The ditriflate $\text{TpRe}(\text{O})(\text{OTf})_2$, **20**, was characterized by X-ray crystallography and found to have both triflates covalently bound.) However, weak Lewis bases such as dimethyl sulfoxide displace the triflate in solvents such as CD_2Cl_2 ; the equilibrium constant was estimated to be $4.9 \times 10^3 \text{ M}^{-1}$ at room temperature. Analysis of the temperature dependence led to estimation of the thermodynamics: $\Delta H^\circ = -12.4$ kcal/mol, and $\Delta S^\circ = -24.8$ cal/(mol·K). The adduct **21** was characterized using solution spectroscopy; as expected,

the pyrazolyl groups are distinct in the ^1H NMR, and the two methyl signals assigned to coordinated DMSO are diastereotopic, downfield of free DMSO, and absent in $(\text{CD}_3)_2\text{SO}$. The IR shows the $\text{Re}-\text{O}$ stretch at 985 cm^{-1} , a band at 858 assigned to ligated $\text{S}-\text{O}$, and the expected bands due to ionic triflate.

This complex shows facile exchange with free Me_2S , shown by reacting $(\text{CH}_3)_2\text{S}$ with labeled d_6 -**21** in CD_2Cl_2 . At -78°C , the exchange process is slow. However, on warming to -50°C (where exchange of coordinated with free DMSO can be shown to be slow), growth of signals due to proteo-**21** is seen. This obeys a first-order approach to equilibrium with $k = 2.31 \times 10^{-4}\text{ s}^{-1}$ at 223 K . This reactivity points to the aryldioxo $\text{Re}(\text{VII})$ complex **22** as the key intermediate; this can be observed by switching to pyridine- N -oxide as the O -atom donor.



The authors note that only 50% of the initial rhenium is observed; they presume conversion to NMR-silent paramagnetic compounds, but provide no further evidence. Addition of Me_2S converts it immediately to **21**; at -50°C the pyridine by-product displaces the DMSO. Warming the complex to 0°C causes formation of three new products. Phenoxy pyridine complex **23** is formed, presumably from carbon migration followed by trapping with pyridine. A phenoxy chloride is also present, rationalized by Cl^- abstraction from solvent. Finally, a catecholate complex **24** is formed, presumably from subsequent oxidation of the initial phenoxy rhenium(V) cation; the proportion of this species increases with increasing concentrations of the N -oxide. Identities of products **23** and **24** were confirmed by independent synthesis. This thus represents the first system where alkyl-to-oxo migration can be directly observed.



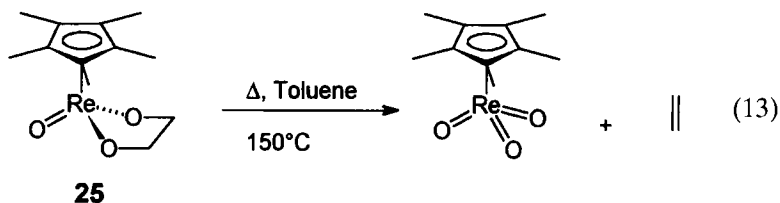
The authors point out that there are a number of cases where such a transformation is thermodynamically feasible but (apparently) kinetically unfavorable. Their rationale centers on the electronic nature of the oxo ligand. An analogy can be drawn between alkyl-to-oxo migration and the migratory insertions observed for alkyl metal carbonyls. The alkyl group migrates with its electrons to an acceptor orbital: $\text{C}=\text{O} \pi^*$ in the case of a migration to CO, $\text{M}=\text{O} \pi^*$ in the case of migration to an oxo. In this case, the electrophilicity of the oxo ligand in TpReO_2Ph is documented by its reaction with organic sulfides. In general, one expects a metal oxo to have a metal-centered LUMO in which the oxo ligand is more nucleophilic, which would explain the general absence of this kind of reactivity.

C. Cycloreversion of Rhenium Diolates

In 1988 Pearlstein and Davison reported that a series of related technetium(VII) trioxo complexes oxidized alkenes to diolate complexes.^{70,71} This was quite similar to the better-known bishydroxylation reaction and opened the possibility that “ OsO_4 equivalents” could be developed using other ligand/metal combinations. One key observation was that the analogous rhenium complexes were not effective oxidants, and because the Re(V) diolates underwent cycloreversion, the reactivity was thermodynamically controlled. Such diol deoxygenations were preceded, though the intermediate metal diolates were usually not isolated or characterized. For example, in the McMurray coupling of ketones with Ti(III) , it is possible to isolate the pinacols, though normally the reaction results in deoxygenation to the alkene.⁷² Schrock and co-workers observed a similar net cycloreversion reaction of a series of tungsten pinacولات⁷³; cycloaddition of al-

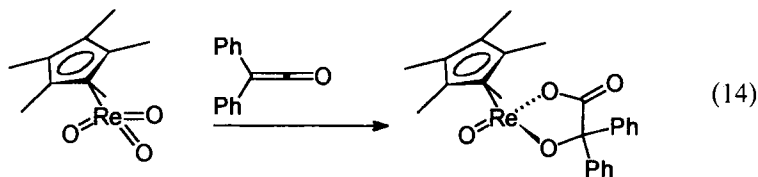
kynes to a metallacyclobutadiene created a new cyclopentadienyl unit. The cyclopentadienyltungsten pinacolate intermediate rapidly cycloreverts to give the observed products, the tungsten dioxo complex plus tetramethylethylene.

The principle that rhenium oxo complexes are thermodynamically incapable of bishydroxylation was also demonstrated in Herrmann *et al.*'s 1986 report of the cycloreversion of alkenes from cyclopentadienyl rhenium(V) diolates. The diolate complex **25** was observed to cyclorevert to Cp^*ReO_3 and ethylene in refluxing toluene, as shown in Eq. (12).⁷⁴ The thio- and dithiodiolate analogs were more stable, but on heating to 200°C produced ethylene (though the thio compounds $\text{Cp}^*\text{ReO}_2\text{S}$ and Cp^*ReOS_2 were not reported to be isolated).



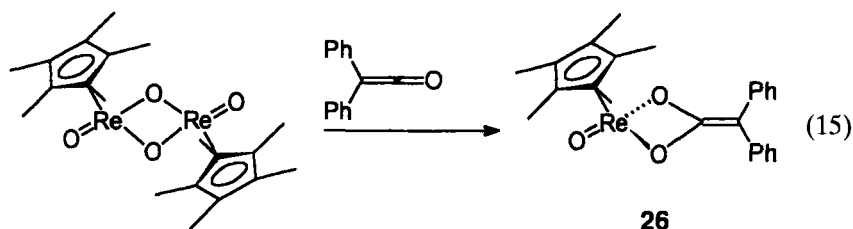
The full-paper follow-up to this initial report⁷⁵ also included nitrogen-substituted metallacycles and imido analogs. None of these systems gave the clean alkene extrusion seen for **25**. Clear structural differences were noted from crystallographic work. In particular, the diolate adopted a puckered-ring geometry in the solid state; placing a nitrogen in place of a ring oxygen caused the ring to flatten considerably. Presumably this was because nitrogen is a better π donor than the diolate oxygen. (One rationale for how this change might affect reactivity is presented later.)

At this point little was known about the thermodynamics of this cycloreversion process. Some hints existed that it was close to thermoneutral, in that ketenes gave a net $[3 + 2]$ cycloaddition to form a "metallalactone" structure, confirmed by X-ray crystallography.⁷⁶ Similar behavior is seen for $(\text{N}^-\text{N})\text{MeReO}_3$ complexes.⁷⁷

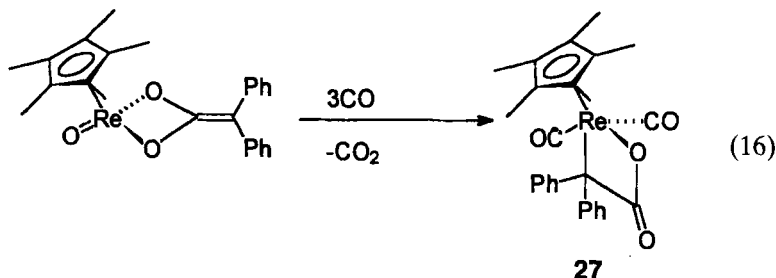


In subsequent work, Herrmann and co-workers isolated two closely related four-membered metallacycles, one of which was formally a metallaoxetane.

Treatment of $(\text{Cp}^*\text{ReO})_2(\mu\text{-O})_2$ with diphenylketene results in $[2 + 2]$ cycloaddition of the carbonyl group to give a dioxametallacycle⁷⁸:

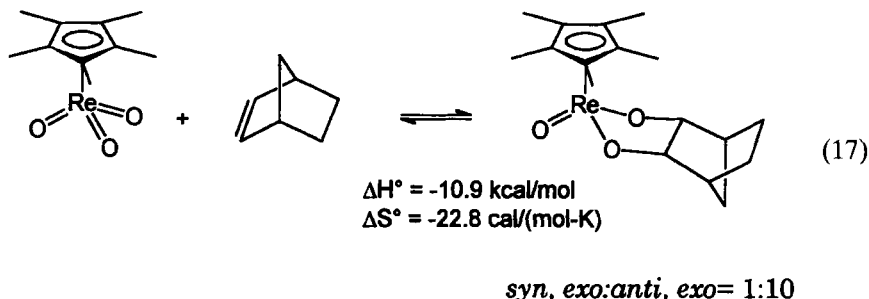


Upon reduction with CO, the terminal oxo ligand is lost as CO_2 , and two CO molecules are incorporated. However, the metallacycle rearranges to place the terminal carbon within the ring:



Crystallographic structure analysis reveals that the rhenium atom in **27** is an extremely distorted four-legged piano stool, with the $\text{Re}-\text{C}$ bond twisting below the plane. The $\text{Re}-\text{C}$ single bond is somewhat long, at 2.29 Å, as is the $\text{Re}-\text{O}$ bond of the metallacycle (2.075 Å), though other bond lengths are normal ($\text{Re}-\text{CO}$ 1.876, 1.935 Å; $\text{C}-\text{C}$ 1.525 Å, $\text{C}-\text{O}$ 1.298 Å, $\text{C}=\text{O}$ 1.191 Å).

The thermochemistry was finally established in 1993, when Gable and Phan reported that norbornene reacted with Cp^*ReO_3 to give an equilibrium mixture of reactants and diolates.⁷⁹ Using the observed equilibrium constant, they calculated that extrusion of unstrained alkenes was an entropy-driven reaction.



The change in strain energy is estimated to be 5.7 kcal/mol,⁸⁰ so oxidation of unstrained alkenes should be thermoneutral to slightly exothermic, but not enough so to overcome the unfavorable change in entropy.

Further work from this group centered on mechanistic investigation of the cycloreversion reaction. The fact that strained alkenes could undergo oxidation provided an experimental variable in evaluation of kinetic behavior. Shea and Kim had recently demonstrated that concerted organic cycloadditions showed characteristic variation of rate with strain in the double bond.⁸¹ This is due to the partial rehybridization of carbon from sp^2 to sp^3 at the transition state. For example, in the cycloaddition of organic azides to strained alkenes, approximately 60% of the strain energy is released at the transition state. The corollary is that concerted extrusions will show a complementary effect, in which the barrier to extrusion increases as the strain energy in the product alkene is increased.

This was not observed in the diolate cycloreversion chemistry (Fig. 4).⁸² The measured (for moderately strained alkenes) and calculated (for more highly strained alkenes) enthalpy of activation for extrusion was approximately constant for a half-dozen examples at 30 ± 1 kcal/mol. (All such examples were disubstituted alkenes to eliminate electronic differences due to substitution.) Oxidations showed the expected decrease in ΔH^\ddagger with increasing strain; the near-unity slope indicates that the reacting carbon is fully sp^3 hybridized in the transition state.

It would have been possible to rescue the concerted hypothesis at this point by claiming that the transition state was structurally similar to the diolate, that is, that the alkene extrusions involved little C—O bond cleavage prior to the transition state. However, the measurement of a significant secondary deuterium kinetic isotope effect ($k_{H4}/k_{D4} = 1.25 \pm 0.05$ at 100°C) gave evidence of significant C—O bond cleavage, whatever the mechanism.

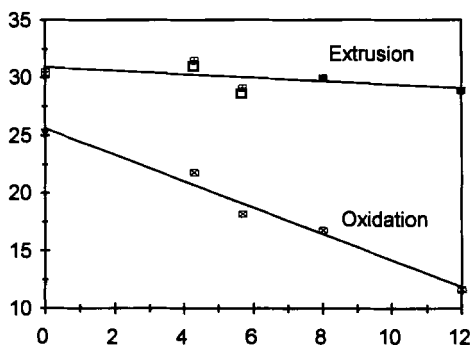
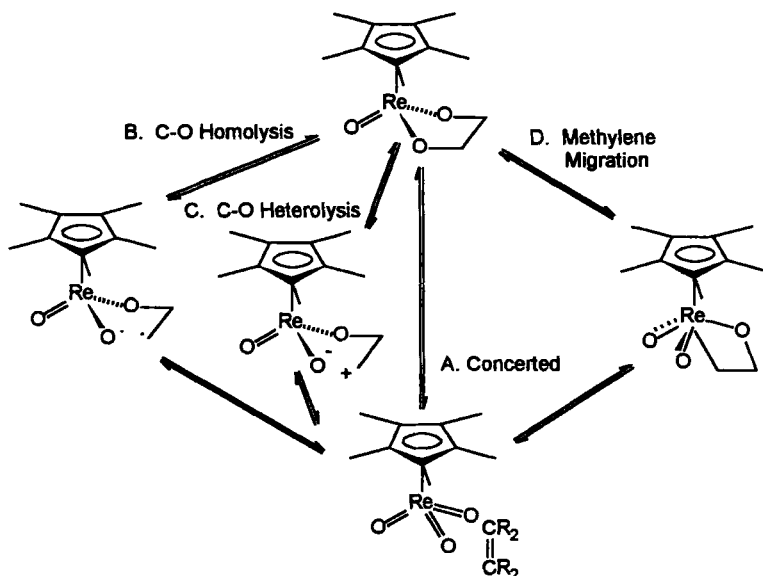


FIG. 4. Activation enthalpies for alkene oxidation and extrusion as a function of strain in the double bond. Legend: \square , \oplus : directly measured activation enthalpies; \blacksquare , \blacktriangledown calculated from the relationship $\Delta H^\ddagger(\text{extrusion}) - \text{double bond strain} - \Delta H^\ddagger(\text{oxidation}) = 5.2 \text{ kcal/mol}$.

This combination of significant C—O bond cleavage and the requirement for sp^3 hybridization served to rule out the classic symmetric concerted transition state. The stereospecificity observed was used to rule out radical and carbocationic intermediates, and the slight increase in ΔH^\ddagger on increasing methyl substitution also argued against these electron-deficient carbon centers being present in the necessary intermediate.

At this point the mechanistic problem was considered in light of Scheme 4. Immediately, paths B and C were excluded on the basis of the stereospecificity of the reaction. Later work on substituent effects (see later discussion) also strongly argued against such intermediates based on their electron deficiency at carbon. Because the strain effects were inconsistent with the concerted fragmentation, path A was ruled out. This left path D, intermediacy of the metallaoxetane, by process of elimination. However, positive evidence for the structure of the transition state was at this point limited.

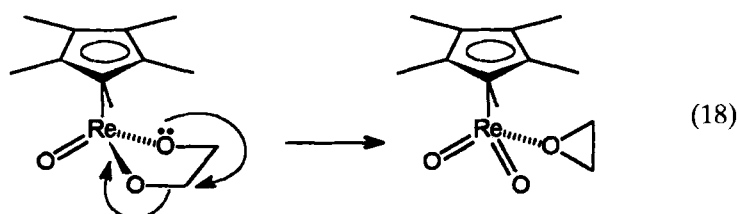
Further work from the Gable group attempted to define more closely the nature of the transition state through structure/reactivity relationships.⁸³ Sequential methyl substitution caused an increase in ΔH^\ddagger of approximately 1.0 kcal/mol per methyl group, regardless of the regio- or stereochemistry of substitution. However, a later paper⁸⁴ reported that for phenyl groups, the number and location were critical to determining the reaction rate. A single phenyl group caused a 2-kcal/mol drop in ΔH^\ddagger . However, for stilbene extrusion from 1,2-diphenylethanediols, ΔH^\ddagger varied considerably between *cis* and *trans* isomers: the slower extrusion of *cis*-stilbene had $\Delta H^\ddagger = 27.8 \text{ kcal/mol}$, whereas extrusion of *trans*-stilbene showed $\Delta H^\ddagger = 24.9 \text{ kcal/mol}$. (It should be noted that these activation parameters are based on observed rate constants; the statistical difference between k_{obs}



SCHEME 4. [Reprinted with permission from Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1994**, *116*, 833–839. Copyright (1994) American Chemical Society.]

and k_{mech} for styrene extrusion has not been accounted for.) One could imagine an “asynchronous concerted” mechanism, in which one C–O bond was almost broken in the transition state, but in which no C–Re interaction was present. This mechanism predicts essentially the same activation enthalpy for styrene and *cis*- and *trans*-stilbene. The observed rates were attributed to an orientational effect, related to that discussed later.

A final possibility was raised by the observation that $(\text{Cp}^*\text{ReO})_2(\mu\text{-O})_2$ deoxygenated epoxides. Migration of carbon not to rhenium but to oxygen would result in a Re(V) –epoxide complex:



The fragmentation of the coordinated epoxide cannot be rate limiting by the same strain effect argument used to exclude the concerted path: this involved rehybridization of carbon to sp^2 . If the migration were the rate-determining pathway, it would be consistent with both the isotope effect and substituent effects, although one might expect a small systematic effect due to ring strain. However, the most likely path for such a rearrangement, backside attack of oxygen on carbon, would result in inversion of stereochemistry, opposite to what is observed. Migration of an electrophilic carbon with retention of configuration is unprecedented; although migration of carbon with its electrons is well known, in this case it would require oxygen to become hypervalent. Also, the cleavage of the coordinated epoxide would then be fairly rapid; such a result would suggest that for the epoxide deoxygenation coordination of the epoxide to the metal would be rate limiting. These arguments were used to exclude rate-limiting migration to O in diolate fragmentations.

All diolate cycloreversions in this system show considerable variation in activation entropy, and this was attributed to an orientational effect. Those diolates that have an eclipsing O—O orientation predominating tend to show a slightly negative activation entropy; those with a predominantly staggered conformation have a significantly positive ΔS^\ddagger . The concerted hypothesis predicts the opposite correlation, that is, an eclipsed conformation should be favorable (with a more positive ΔS^\ddagger and a lower ΔG^\ddagger), because of the predisposed alignment of the orbitals that interact in making the incipient C=C bond. The metallaoxetane hypothesis suggests that orientation of the cleaving C—O bond with an empty orbital at the metal is critical. Indeed molecular orbital calculations (extended Hückel, HF *ab initio*) confirm that the LUMO is primarily M=O π^* in character, with the metal d component possessing a lobe directed parallel to one C—O bond in an eclipsed conformation (Fig. 5).

This discovery suggested an orbital-based rationale for the migration barrier. In the diolate cycloreversions, the transition state involves developing an interaction between the filled C—O bond and the empty metal d component of the LUMO. This results in formation of the new M—C bond as the C—O bond breaks; carbon migrates with this pair of bonding electrons. The oxygen formally is left with an empty orbital, but recall that in the diolate the metal formally has a d^2 configuration. (The HOMOs of the diolate were found to be primarily oxygen lone pairs; the metal "lone pair" was not readily apparent.) The metal can donate electrons to form the new M=O π -bond as the reaction proceeds. Indeed, one finds that calculations at various levels of theory show the LUMO of **25** to have the appropriate symmetry; that derived from EHMO calculations is shown in Fig. 6. Based on perturbation MO theory,⁸⁵ one expects that control of the

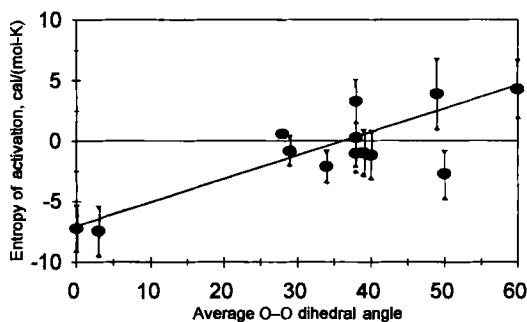


FIG. 5. Relationship between average solution O-C-C-O dihedral for diolates and the ΔS^\ddagger for cycloreversion to Cp^*ReO_3 and alkene. Error bars are 95% confidence limits. [Reprinted with permission from Gable, K. P.; Juliette, J. J. *J. Am. Chem. Soc.* **1995**, *117*, 955–962. Copyright (1995) American Chemical Society.]

energetics of the reaction lie primarily in (i) spatial overlap of the orbitals, dictated by readily accessible geometries of the diolate ring; and (ii) relative energies of the interacting orbitals. A C–O bonding orbital will not change appreciably from structure to structure. However, the energy of the LUMO is undoubtedly a variable that depends on the ligand environment and

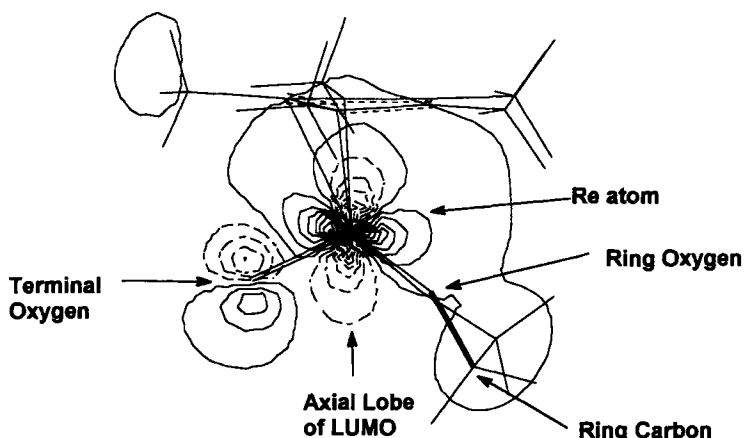


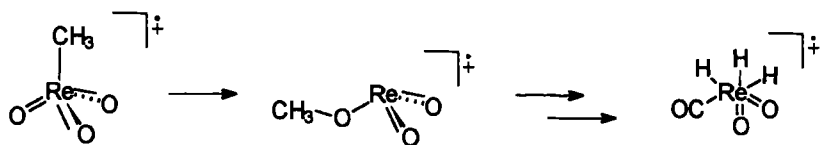
FIG. 6. Diagram of the LUMO of Cp^*ReO_3 . Note the alignment of one C–O bond with the lobe of the metal orbital *trans* to the Cp^* ring. [Adapted with permission from Gable, K. P.; Juliette, J. J. *J. Am. Chem. Soc.* **1996**, *118*, 2625–2633. Copyright (1996) American Chemical Society.]

geometry of the metal center. Further, it is possible that the energy of the metal d electrons plays a role.

This hypothesis also rationalizes the low reactivity of substrates with flattened rings. In these cases, the C—X bond that would have to cleave is oriented along the node of the LUMO, and thus, spatial overlap between the C—X bonding electrons and the acceptor orbital is poor.

In considering alkene oxidation as the microscopic reverse of this extrusion reaction, one may simply turn around the logical arguments just presented. The interaction of a metal alkyl bond with an acceptor orbital on oxygen will be controlled by whether the acceptor orbital (in this case, the $M=O \pi^*$) is low enough in energy to provide transition state stabilization. The argument is congruent with the Brown/Mayer hypothesis concerning the electrophilicity of the oxo fragment.

An intriguing application of this hypothesis may have been observed in the mass spectrometric behavior of MTO.⁸⁶ Loss of H_2 and CO from the parent ion were the major processes observed in both metastable ion and collisional activation mass spectrometry. Both were viewed as unusual; the latter, in particular, required a rationale for forming a C—O bond. The authors proposed migration of carbon to oxygen in the parent ion to form a methoxyrhenium complex of the same mass, followed by sequential back migration of the hydrogens:



(19)

The latter complex can then either reductively eliminate H_2 or lose CO. If, indeed, the methoxy species is responsible for the entry into this manifold, then it appears that the ionization of MTO (whose most available electrons have been shown to lie on oxygen⁸⁷) creates the necessary electrophilicity at oxygen needed to facilitate the alkyl migration.

All of these studies have mechanistic implications for osmylation and for the design of new reagents for alkene oxidation. It remains to be seen whether the mechanism that is apparently operating for rhenium diolate cycloreversion is a general phenomenon that explains the cycloaddition of alkenes to the L_nMO_2 unit. The molecular-orbital picture describing the nature of the alkyl migration from metal to oxygen offers some clues as to where to seek this kind of process, but again the generality of its predictions remains to be demonstrated.

IV

CONCLUSIONS

Over the past 10 years, a large array of chemical transformations has been developed for high-valent oxygenates of the metals technetium and rhenium. Detailed mechanistic inquiries into the mechanisms of these transformations has shed light on several long-standing problems in organic oxidation chemistry and has revealed the importance of important structural classes of metal oxo and peroxo complexes. In several cases, preparatively useful new chemistry has been developed from these observations. The field thus crosses the boundaries of preparative synthetic organic chemistry, structural inorganic chemistry, and mechanistic organic, inorganic, and organometallic chemistry.

In both the case of epoxidations via η^2 -peroxides and that of diolate cycloreversion, chemists must exercise caution that the mechanistic lessons learned for rhenium may not translate to processes mediated by other metals, ligands, or oxidation states. This has always been a particular problem in mechanistic organometallic chemistry. However, it is likely that systems can be developed based on the observations described here that can discern the structural features that control competing mechanistic manifolds.

ACKNOWLEDGMENTS

I am particularly grateful to Profs. James Espenson and James Mayer for sharing preprints of their work. I also thank Prof. Wolfgang Herrmann for permission to use Figs. 1 and 3. Work performed at Oregon State University was accomplished with the generous support of the National Science Foundation, and of the donors to the Petroleum Research Fund, administered by the American Chemical Society.

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(1-Alkynyl)carbene Complexes (= 1-Metalla-1-buten-3-yne): Tools for Synthesis

RUDOLF AUMANN and HUBERT NIENABER

*Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität
48149 Münster, Germany*

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I

INTRODUCTION

The usefulness of Fischer carbene complexes^{1,2} to organic synthesis has been amply demonstrated over the past several decades. Several reviews have been published covering both thermal³ and photochemical⁴ reactions of such compounds with a broad array of various organic functional groups. Most prominently, reactions of α,β -unsaturated carbene complexes with a C=C bond, mainly of (1-alkenyl)carbene and arylcarbene complexes with alkynes, have found wide application in organic synthesis.⁵⁻¹² Much less attention has been paid thus far to the inherent synthetic potential of α,β -unsaturated compounds with a C \equiv C bond, namely (1-alkynyl)carbene complexes.¹³ The aim of this review is to focus on the aspect of reactivity of (1-alkynyl)carbene complexes, especially if a regio- and/or stereoselective formation of C,C- or C,X bonds is achieved that might be profitably utilized in organic synthesis. Alkynylcarbene complexes of the nonconjugated type, in which an alkynyl group is tethered to the carbene carbon atom by a saturated carbon atom, a carbon chain, or a heteroatom, have not been included in this review. Though the scope of information to date is somewhat limited and for most cases can be exemplified by reactions of compounds of type $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}\equiv\text{CR}$ (M = Cr, W) only, it appears to us that at least some reaction paths that have been unraveled thus far are startling and deserve to be summarized in a review for an interested readership.

II

PREPARATION, SPECTROSCOPIC AND STRUCTURAL DATA

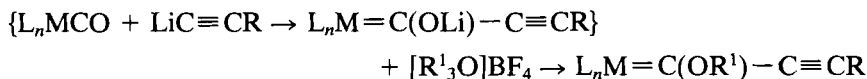
Typical modes for the preparation of (1-alkynyl)carbene complexes, as well as spectroscopic and structural data, are briefly summarized. Alkoxy- and amino(1-alkynyl)carbene complexes are available from metal carbonyls and metal isocyanides, respectively.

A. Alkoxy(1-alkynyl)carbene Complexes

Alkoxy(1-alkynyl)carbene ligands are obtained either by addition of an alkynyl group to a carbonyl ligand or by transformation of a carbene ligand by generation of an alkyne unit.

1. Alkoxy(1-alkynyl)carbene Complexes via the Fischer Route

The preparation of alkoxy(1-alkynyl)carbene complexes (e.g., of compounds $L_nM=C(OR^1)-C\equiv CR$) mostly follows the two-step Fischer procedure,¹⁴ involving addition of a 1-lithio alkyne $LiC\equiv CR$ to a metal carbonyl $L_nM(CO)$ to give a metal acylate $L_nM=C(O^-\text{Li}^+)-C\equiv CR$ ¹⁴, which is subsequently alkylated with an oxonium salt $[R^1_3O]BF_4$,¹⁵ an alkyl triflate $R^1OSO_2C-CF_3$,^{16,22} or an alkyl fluorosulfonate R^1O_3SF ^{16a,17}:



Some examples of such compounds, including typical spectroscopic data, are given in Table I.

Because metal carbonyls as well as 1-lithio alkynes³¹ are readily available, a wide variety of (1-alkynyl)carbene complexes can be obtained via the Fischer route in a procedure³² similar to that given for $(CO)_5Cr=C$

TABLE I
¹³C NMR SHIFTS (δ VALUES, $CDCl_3$) AND IR FREQUENCIES (cm^{-1}) OF SELECTED
ALKOXY(1-ALKYNYL)CARBENE COMPLEXES $L_nM=C(OR^1)C\equiv CR$

ML_n	R^1	R	$\delta(C1)$	$\delta(C2)$	$\delta(C3)^a$	$\nu(C\equiv C)$	Pp	Ref. ^b	Ref. ^c
$Cr(CO)_5$	OEt	Ph	314.1	91.9	135.5	2154	^d	18, 19, 20, 21	21
$CrCp(CO)(NO)$	OEt	Ph	307.2 306.5 ^e	92.2 88.4	^e	2152	^f	22	22
$Mo(CO)_5$	OEt	Ph	^e	^e	^e	^e	^e	23	
$MoCp(CO)(NO)$	OMe	<i>p</i> -Tol	292.0	97.5	130.6	^e	^d	24	24
$W(CO)_5$	OEt	Ph	286.1	97.2	130.0	2156	^d	18, 19	25
$MnPh_3Sn(CO)_4$	OMe	Ph	^e	^e	^e	^e	^d	26	
$Mn(\eta^5-C_5Cl_5)(CO)_2$	OMe	$[Re]C\equiv C^h$	288.9	82.4 ^h	127.4 ^h	^h	^d	27	
$MnCp(CO)_2$	OMe	$[Re]^h$	283.9	^e	^e	1968	^d	28	
$Re_2(CO)_9$	OMe	$[Re]^h$	^e	^e	^e	^e	^d	29	
$Fe(CO)_4$	OEt	Ph	280.5	95.9	121.3	2190	^d	30	
$Fe(CO)_4$	OEt	SiMe ₃	280.8	107.3	132.5	2200	^d	30	
$FeCp(CO)_2$	OMe	SiMe ₃	290.8	105.4	149.0	2117	ⁱ	38b	

^a Based on a ¹³C labeling study, the β -acetylenic carbon atom C3 is more deshielded than the α -acetylenic carbon atom C2.^{17a}

^b Reference for preparation.

^c Reference for spectroscopic data.

^d Alkylation with an oxonium salt.

^e Not reported.

^f Alkylation with alkyl triflate.

^g Two different rotamers.

^h $[Re] = (C_5Me_5)Re(NO)(PPh_3)$.

ⁱ Alkylation with a carboxonium salt.

(OEt)–C≡CPh. As an example, Cr(CO)₆ (5.50 g, 25.00 mmol) is placed in a 100-ml two-neck flask fitted with an efficient stirrer bar and a 100-ml dropping funnel. After the apparatus has been flushed with argon, phenylacetylene (3.06 g, 30.00 mmol) and dry THF (50 ml) is placed into the dropping funnel, and a solution of *n*-BuLi (27.00 mmol, 16.88 ml of a 1.6 M solution in hexane) is added dropwise at 20°C, while a slow stream of argon is passed through the solution to achieve efficient mixing. After 15 min at 20°C, the solution of phenylalkynyl lithium thus generated is added dropwise within 15 min to the Cr(CO)₆ with rapid stirring. A clear orange solution is obtained. Cr(CO)₆ will be dissolved completely after approximately 80% of the reagent has been added. Evaporation to dryness (20°C, 20 torr) gives a bright yellow solid, from which the remaining THF is removed at 1 torr, 20°C. The residue is dissolved in dry dichloromethane (50 ml) and the solution is cooled to –78°C. Triethyloxonium tetrafluoroborate (7.59 g, 40.00 mmol) in dry dichloromethane (10 ml) is added at –78°C with rapid stirring. A dark mixture is formed immediately, which is brought to dryness (20°C, 20 torr). The residue is extracted efficiently four times, with 50 ml of Et₂O each time, to leave a grayish residue of LiBF₄. Crystallization from pentane at –78°C affords (CO)₅Cr=C(OEt)–C≡CPh (7.00 g, 80% black-violet platelets).¹⁸

An alkoxy(1-alkynyl)carbene complex (CO)₅W=C(OEt)–C≡CH with a terminal hydrogen substituent has been mentioned but not fully characterized thus far.⁴² For side reactions of 1-alkynyl acylmetallates, see Section VI.

Reaction of lithium 1-ethoxyacetylide LiC≡COEt with L_nM(CO) [L_nM = (CO)₅Cr, (CO)₅Mo, (CO)₅W, (CO)₄Fe] quite unexpectedly affords dialkoxycyclopropenyldiene complexes^{33,34} in high yield, e.g., {(CO)₆Cr + LiC≡COEt} + [Et₃O]BF₄ → (CO)₅Cr=C(EtOC=COEt).

Lithium 1-aminoacetylides LiC≡CNR₂ give alkoxy aminocyclopropenyldiene chromium complexes,³⁴ though in low yield.

The reaction of lithium alkynes also may lead to production of vinylidene complexes by elimination of carbon monoxide,^{22,24,35} e.g., {Cp(NO)(CO)₂M + LiC≡CR} → [Cp(NO)(CO)M–C≡CR]Li + Cp(NO)(CO)M=C(OLi)–C≡CR} + [Me₃O]BF₄ → Cp(NO)(CO)M=C=CRMe + Cp(NO)(CO)M=C(OMe)–C≡CR.

2. Alkoxy(1-alkynyl)carbene Complexes via Alkoxy(methyl)carbene Complexes

Alkoxy(1-alkynyl)carbene complexes also are obtained by condensation of (1-ethoxy)methylcarbene complexes with *bulky* acyl chlorides as side products (10–12% yield) together with [(2-acyloxy)ethenyl]carbene complexes (50–78% yield),³⁶ e.g., (CO)₅M=C(OEt)–CH₃ + 3 RCOCl + 3 Et₃N → (CO)₅M=C(OEt)–C≡CR (M = Cr, W; R = *t*-Bu, *c*-Pr).

3. *Alkoxy(1-alkynyl)carbene Complexes via Alkoxy(2-aminoethenyl)carbene Complexes*

Aminomethylenation of [2-(*NH*-amino)ethenyl]carbene complexes affords alkoxy(1-alkynyl)carbene complexes (22–30% yield) by β -elimination, together with [2-amino-1-(iminoacyl)ethenyl]carbene complexes (61–83% yield),³⁷ e.g., $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{CPh}(\text{NPh}) + \text{HCONR}_2 + \text{POCl}_3/\text{Et}_3\text{N} \rightarrow (\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}\equiv\text{CPh}$ ($\text{M} = \text{Cr}, \text{W}$; $\text{R} = \text{pyrrolidine, morpholine}$).

4. *Alkoxy(1-alkynyl)carbene Complexes via Acylation of Metallates*

Synthesis of cationic alkoxy(1-alkynyl)carbene iron complexes is achieved by acylation of $\text{Cp}(\text{CO})_2\text{Fe}^-$ with an anhydride and subsequent alkylation of the acyl derivative,³⁸ e.g., $\{\text{CpFe}(\text{CO})_2\}^- + \text{C}_4\text{H}_9\text{OCO}_2-\text{COC}\equiv\text{CPh} \rightarrow \text{CpFe}(\text{CO})_2-\text{COC}\equiv\text{CPh} + [(\text{MeO})_2\text{CH}]\text{PF}_6 \rightarrow \text{Cp}(\text{CO})_2\text{Fe}=\text{C}(\text{OMe})-\text{C}\equiv\text{CPh}^+$.

B. *Amino(1-alkynyl)carbene Complexes via Isocyano Compounds*

Amino(1-alkynyl)carbene complexes are available by aminolysis of ethoxy(1-alkynyl)carbene complexes (see Section IV). Generation of amino(1-alkynyl)carbene complexes $(\text{CO})_5\text{Cr}=\text{C}(\text{NR}^1\text{E})-\text{C}\equiv\text{CR}$ from isocyano complexes $(\text{CO})_5\text{Cr}(\text{CNR}^1)$ is recommended, if aryl amines or bulky aliphatic amines are to be introduced as substituents, in which case aminolysis of the corresponding alkoxy- or acyl(1-alkynyl)carbene complexes³⁹ would lead to production mainly of (2-aminoethen-1-yl)carbene or allenylidene complexes (vide infra), e.g., $\{(\text{CO})_5\text{Cr}(\text{CNR}^1) + \text{LiC}\equiv\text{CR} \rightarrow (\text{CO})_5\text{Cr}=\text{C}(\text{NR}^1\text{Li})-\text{C}\equiv\text{CR}\} + \text{EX} \rightarrow (\text{CO})_5\text{Cr}=\text{C}(\text{NR}^1\text{E})-\text{C}\equiv\text{CR}$. The reaction follows a two-step procedure, in which *N*-lithio iminoacylates $(\text{CO})_5\text{Cr}=\text{C}(\text{NR}^1\text{Li})-\text{C}\equiv\text{CR}$ are generated in a first step by addition of 1-lithio alkynes $\text{LiC}\equiv\text{CR}$ ($\text{R} = \text{Ph}, \text{SiMe}_3$) to $(\text{CO})_5\text{Cr}(\text{CNR}^1)$ ($\text{R} = \textit{c}\text{-C}_6\text{H}_{11}, \text{Ph}, \textit{p}\text{-MeC}_6\text{H}_4, \textit{o}\text{-MeC}_6\text{H}_4$). Protonation and alkylation, respectively, of the iminoacylate with EX $\{\text{H}_2\text{O}, \text{MeI}, [\text{Et}_3\text{O}]\text{BF}_4, \text{BrCH}_2-\text{CH}(-\text{O}-)\text{CH}_2\}$ produces amino(1-alkynyl)carbene complexes $(\text{CO})_5\text{Cr}=\text{C}(\text{NR}^1\text{E})-\text{C}\equiv\text{CR}$ in 75–90% overall yield.⁴⁰ The latter compounds are generated stereoselectively in the *E* configuration (*E/Z* = 14:1 to 29:1) by kinetic reaction control and isomerize at 80°C to give the corresponding *Z* stereoisomers as main products. Alkylation of *N*-aryl compounds $(\text{CO})_5\text{Cr}=\text{C}(\text{NArLi})-\text{C}\equiv\text{CR}$ ($\text{Ar} = \text{Ph}, \textit{p}\text{-MeC}_6\text{H}_4, \textit{o}\text{-MeC}_6\text{H}_4$) yields amino-carbene complexes predominantly of the *Z* configuration by kinetic reaction control.⁴⁰ Stereocontrol in the introduction of substituents on the nitrogen

TABLE II
¹³C NMR SHIFTS (δ VALUES, CDCl₃) AND IR FREQUENCIES (cm⁻¹) OF SELECTED
 AMINO(1-ALKYNYL)CARBENE COMPLEXES L_nM=C(NR¹R²)C≡CR

ML _n	R ¹	R ²	R	δ (C1)	δ (C2)	δ (C3)	ν (C≡C)	Ref. ^b
Cr(CO) ₅	Et	Cy	Ph	246.5	91.5	123.0	2165	40
Cr(CO) ₅	Cy	Et	Ph	245.0	91.4	122.8	2165	40
Cr(CO) ₅	Et	Cy	SiMe ₃	249.8	105.5	140.2	2155	40
Cr(CO) ₅	Me	Cy	H	249.6	83.5	118.2	2158	40
Cr(CO) ₅	Cy	Me	H	248.2	84.2	116.9	2158	40
Cr(CO)(NO)Cp	Me	Me	Ph	262.7	89.8	123.1	2171	22
W(CO) ₅	Allyl	Allyl	Ph	230.4	92.8	126.5	2170	39
W(CO) ₅	Me	Me	SiMe ₃	230.8	106.1	134.2	^a	42
W(CO) ₅	Me	Me	H	231.1	85.9	112.9	^a	42
W(CO) ₅	Me	NHMe	Ph	212.3	89.1	123.1	2171	46
W(CO) ₅	NHMe	Me	Ph	212.1	91.6	122.5	2173	46

^a Data not reported.

^b Reference for preparation and spectroscopic data.

atom of an amino(1-alkynyl)carbene complex also can be achieved by a proper sequential aminolysis of alkoxy(1-alkynyl)carbene complexes with a primary amine (vide infra) followed by treatment of the resulting (NH)-carbene complex with Cs₂CO₃ in the presence of the desired electrophile.⁴¹ Some examples of amino(1-alkynyl)carbene complexes, including typical spectroscopic data, are given in Table II. Because of the strong contribution of the iminium ylide structure, e.g., ⁻(OC)₅Cr-C(=N⁺R¹R²)-C≡CR, the ¹³C NMR signal of the carbene carbon atom of an amino(1-alkynyl)carbene complex, e.g., (OC)₅Cr=C(NR¹R²)-C≡CR (Table II), is shifted upfield (by 60–70 ppm) compared to that of the corresponding ethoxy(1-alkynyl)carbene complex (Table I). Further indication for an iminium structure is given by the elongation of the Cr=C as well as the C(carbene)-C bond distances (Table III), and by the fact that stable *E/Z* stereoisomers at the C=N bond are formed (Table II).

Much attention has been focused recently on the preparation of parent alkynylcarbene complexes (CO)₅M=C(NR₂)-C≡CH (M = Cr, W; R = Me^{20,42} CH₂CH=CH₂⁴³) having a terminal alkynyl group. Concern over the assignment of structures was raised by controversial reports of an allenylidene (CO)₅Cr=C=C=CH(NMe₂) as well as an alkynyl structure (CO)₅Cr=C(NMe₂)-C≡CH, based on spectroscopic evidence. The presence of a C²≡C³H moiety in, for example, (CO)₅Cr=C(NRCy)-C≡CH (R = H, Me) is unambiguously proven by the coupling constants *J*(C,H) { δ 118.2 [CH, ¹*J*(C,H) = 255 Hz, C3], 83.5 [Cq, ²*J*(C,H) = 48 Hz, C2]}.⁴⁰

TABLE III
SELECTED BOND DISTANCES OF (1-ALKYNYL)CARBENE COMPLEXES

	<i>d</i> M=C [pm]	<i>d</i> C—C [pm]	<i>d</i> C≡C [pm]	Ref.
(CO) ₅ Cr=C(OEt)C≡CPh	200(2)	137(3)	119(3)	44
(CO) ₅ Cr=C(NMeCy)C≡CH	211.7(3)	144.4(4)	118.1(5)	40
(CO) ₅ Cr=C(NEtCy)C≡CPh	210.0(2)	142.7(3)	119.9(3)	40
(CO)(NO)(Cp)Mo=C(OMe)C≡CTol	204.3(3)	142.5(5)	119.9(5)	45
(CO) ₅ W=C(NMe ₂)C≡CSiMe ₃	^a	^a	^a	42
(CO) ₅ W=C(OMe)C≡CRe (η ⁵ -C ₅ Me ₅)(NO)(PPh ₃)	220.0(8)	138(1)	123(1)	28
(CO) ₅ W=C(NMe—NHMe)C≡CPh	223.9(7)	143.9(10)	118.6(10)	46
(CO) ₅ W=C(NH—NMe ₂)C≡CPh	221.0(6)	142.7(9)	119.7(10)	46
(CO) ₂ (Cp)Fe=C(NH—Tol)C≡CSiMe ₃] ⁺	194.0(5)	143.0(8)	118.6(8)	38b

^a Not reported in the original paper.

Also, X-ray structure analyses of (CO)₅Cr=C(NMeCy)—C≡CH and of other (1-ethyne)carbene complexes have been reported (see Table III).

III

REACTION WITH CARBON NUCLEOPHILES (AND HOMOLOGS)

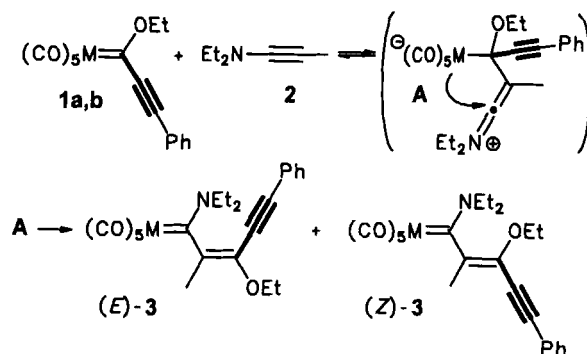
The addition of a carbon nucleophile to a (1-alkynyl)carbene complex (CO)₅M=C(OEt)—C≡CR can be expected to occur either at the M=C or at the C≡C bond.

A. 1-Metalla-1,3-hexadien-5-yne

Although many examples of addition reactions of carbon nucleophiles to the C≡C bond of a (1-alkynyl)carbene complex have been reported (vide infra), to date there are few reports of reactions by which a carbon-carbon bond is formed to C1, thus leaving the C≡C bond unchanged. Reactions of the latter type involve insertion of an alkyne into the M=C bond of a (1-alkynyl)carbene complex **1** (Scheme 1).

1. 1-Metalla-1,3-hexadien-5-yne by Insertion of Electron-Rich Alkynes into the M=C Bond of a (1-Alkynyl)carbene Complex

Insertion of an alkyne into the M=C bond of compound **1** may proceed in two different modes that lead to different compounds, depending upon



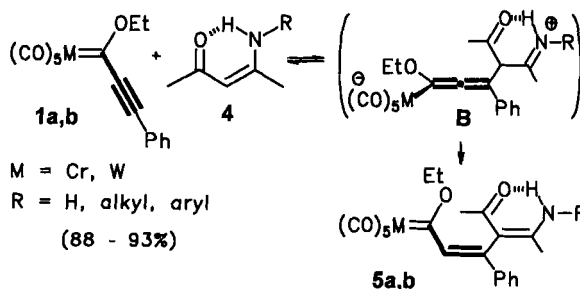
$\text{M} = \text{Cr}$ (*E/Z*)-**3** = 69/2 %; W (*E/Z*)-**3** = 73/3 %

SCHEME 1. 1-Metalla-1,3-hexadien-5-ynes.

the nature of the substituents of each reaction partner. Dötz-type reactions,^{3,5} which afford 1,4-dioxynaphthalenes or indenes, are initiated by the exchange of a *cis* carbon monoxide ligand of the $(\text{CO})_5\text{Cr}$ moiety for an alkyne, and subsequently by a regioselective insertion of the alkyne into the $\text{M}=\text{C}$ bond to produce a *chelate compound*, a 3,4- η^2 -1-metalla-1,3,5-hexatriene,^{47,222} which may either undergo insertion of carbon monoxide into the $\text{M}=\text{C}$ bond or form a cyclization product without insertion of carbon monoxide. Thus far, reactions of this type have not been reported for (1-alkynyl)carbene complexes **1**, but a different type of alkyne insertion into the $\text{M}=\text{C}$ bond of (1-alkynyl)carbene complexes has been observed. It appears to occur without prior loss of a *cis* carbon monoxide ligand and involves nucleophilic addition of an (electron-rich) alkyne, e.g., 1-amino or 1-alkylthio alkynes, to the carbene carbon atom with formation of a zwitterionic adduct **A**, from which an *open-chain compound*, a 1-metalla-1,3-hexadien-5-yne (*E/Z*)-**3**, is generated by 1,3-migration of the metal unit (Scheme 1).^{48,49} Alkyne addition to the $\text{C}\equiv\text{C}$ bond of a (1-alkynyl)carbene complex has not been observed thus far, whereas Michael-type addition of an electron-rich alkyne to the $\text{C}=\text{C}$ bond of a (1-alkenyl)carbene complex has been reported.⁴⁸

B. 1-Metalla-1,3,5-hexatrienes, Formation and Cyclization Reactions

1-Metalla-1,3,5-trienes $\text{M}=\text{C}-\text{C}=\text{C}-\text{C}=\text{C}$ play a pivotal role in many applications of carbene complexes to organic synthesis. These compounds are readily available from methylcarbene complexes (by condensation, e.g. with α,β -unsaturated aldehydes), from 1-metalladienes (by insertion of an



SCHEME 2. 6-Amino-1-metalla-1,3,5-trienes.

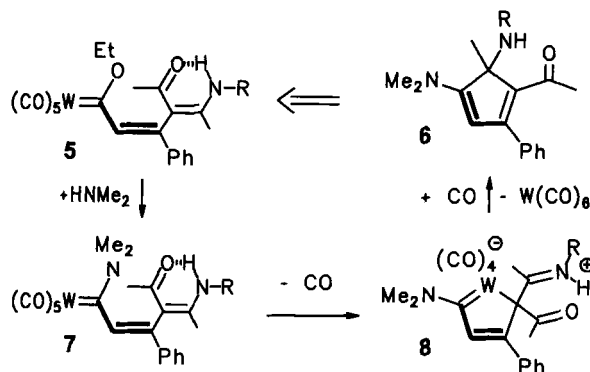
alkyne into the $\text{M}=\text{C}$ bond), by metathesis of 1-metalla-1,3-dienes or related compounds, and by addition of enamines to the $\text{C}\equiv\text{C}$ bond of a (1-alkynyl)carbene complex.

1. 6-Amino-1-metalla-1,3,5-hexatrienes by Addition of an Enamine to the $\text{C}\equiv\text{C}$ Bond of a (1-Alkynyl)carbene Complex

In contrast to 1-amino *alkynes*, which add to the $\text{M}=\text{C}$ bond of a (1-alkynyl)carbene complex **1** (vide supra), 1-amino *alkenes* (enamines) add to the $\text{C}\equiv\text{C}$ bond of compounds **1**. The latter reaction may yield different products depending on the substituents and the reaction conditions. Open-chain secondary (*NH*)-enamin-3-ones **4** undergo a *C*-addition to (1-alkynyl)carbene complexes **1a,b** ($\text{M} = \text{Cr}, \text{W}$) and afford open-chain conjugated 1-metalla-1,3,5-trienes **5a,b** (= 1-butadienyl carbene complexes), which have been isolated as crystals and characterized both spectroscopically and by X-ray structure analyses (Scheme 2).⁵⁰ The key step of this reaction involves formation of an allene-type intermediate **B** and a 1,3 hydrogen transfer from the α -carbon atom of the carbonyl group to the central carbon atom of the allene unit. In competition with the formation of conjugated 1-metalla-1,3,5-trienes **5a,b** from intermediates **B**, nonconjugated open-chain 1-metalla-1,3,6-heptatrienes are also produced by an "ene"-type reaction.^{56b}

2. 2-Amino-1-metalla-1,3,5-hexatrienes

Conjugated 2-alkoxy-6-amino-1-metalla-1,3,5-hexatrienes of type $\text{M}=\text{C}(\text{OR})-\text{C}=\text{C}-\text{C}=\text{C}(\text{NR}_2)$ are most easily accessible by addition of enamines to alkoxy(1-alkynyl)carbene complexes in a broad array of different substituents. Due to the highly unsaturated character of such compounds a variety of transformations into organic products can be anticipated. Since

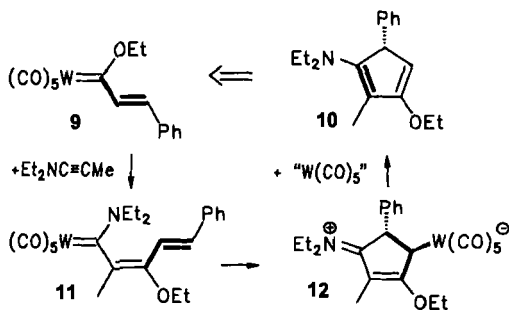


SCHEME 3. Cyclopentadienes via cyclization of 2-amino-1-metalla-1,3,5-trienes.

reactivity of 2-alkoxy- and 2-amino-1-metalla-1,3,5-hexatrienes is characteristically different, both groups of compounds will be discussed separately.

a. *Cyclopentadienes via 2-amino-1-metalla-1,3,5-hexatrienes by [3+2] cycloaddition of the $\text{C}-\text{C}\equiv\text{C}$ unit of a (1-alkynyl)carbene complex to the $\text{C}=\text{C}$ bond of an enamine ("enamine route").* Electrocyclic ring closure of 2-amino-1-metalla-1,3,5-hexatrienes has been shown to occur smoothly and leads to formation of cyclopentadiene complexes, and finally (metal-free) cyclopentadienes.^{12c} Thus, for example, cyclopentadienes **6** are obtained from 2-ethoxy-1-(pentacarbonyl)tungsta-1,3,5-hexatrienes **5** ($\text{R} = i\text{-Pr}, t\text{-Bu}$) in two steps involving aminolysis of **5** with formation of a 2-amino-1-(pentacarbonyl)metalla-1,3,5-hexatriene **7**, and a subsequent cyclization/fragmentation (Scheme 3). Thermally induced cyclization of 1-(pentacarbonyl)metalla-1,3,5-trienes **7** affords a tetracarbonyl chelate complex initially, which does not exhibit π coordination as might have been anticipated, but instead possesses a novel 1-metalla-cyclopentadiene iminium-ylide structure **8**. Amino-1-metalla-1,3,5-trienes **7** and iminium-ylide complexes **8** were both isolated and have been fully characterized by X-ray structure analyses.⁵¹

b. *Cyclopentadienes via 2-amino-1-metalla-1,3,5-hexatriene by [3+2] cycloaddition of the $\text{C}-\text{C}\equiv\text{C}$ unit of a 1-metalla-1,3-diene to the $\text{C}\equiv\text{C}$ Bond of an alkyne ("alkyne route").* An alternative route to the formation of cyclopentadienes by [3+2] cycloaddition, other than that shown in Scheme 3, is based upon the formation of a 1-metalla-1,3,5-triene by insertion of the $\text{C}\equiv\text{C}$ bond of an alkyne ("alkyne route") into the $\text{M}=\text{C}$ bond of a (1-alkenyl)carbene complex (= 1-metalla-1,3-diene). This latter process

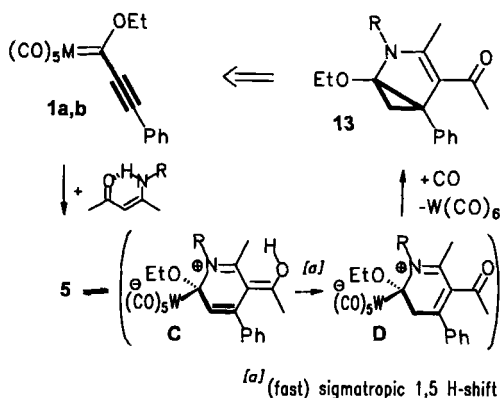


SCHEME 4. Cyclization of 2-amino-1-metalla-1,3,5-trienes to cyclopentadienes via η^1 cyclopentadiene complexes.

is illustrated by the regioselective insertion of the 1-aminoalkyne $Et_2NC\equiv CMe$ into the $M=C$ bond of metalladiene **9** to give a 1-tungstena-1,3,5-hexatriene **11**, which has been characterized by X-ray analysis.⁴⁸ Compound **11** undergoes smooth ring closure under very mild conditions ($t_{1/2} = \text{ca. } 14 \text{ h, } 20^\circ\text{C}$) without loss of carbon monoxide to yield a (novel) zwitterionic η^1 -cyclopentadiene complex **12**, whose structure has been elucidated by X-ray analysis.^{12c} A cyclopentadiene **10** is finally obtained by thermally induced disengagement of the metal unit from complex **12** (Scheme 4). A variety of processes involving formation of a cyclopentadiene moiety from pentacarbonyl (1-alkenyl)carbene complexes with alkynes exist.^{3r,9a,9h} These processes are based upon the annulation of a $C-C=C$ unit of a 1-metalla-1,3-diene to a $C\equiv C$ bond of an alkyne. 1-Metalla-1,3,5-hexatrienes, formed from insertion of the alkyne into the $M=C$ bond, may be assumed to be a key intermediate (vide infra). It is important to note that the regiochemistry of the $[3+2]$ cycloaddition of a (1-alkynyl)carbene complex to an enamine ("enamine route") is complementary to that shown in Scheme 4 ("alkyne route"). For a different route to amino cyclopentadienes via the intermediate formation of 6-amino-1-metalla-1,3,5-trienes (instead of 2-amino-1-metalla-1,3,5-trienes), see Scheme 35.

3. 2-Alkoxy-1-metalla-1,3,5-hexatrienes

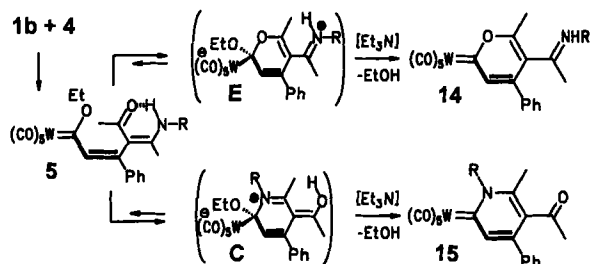
In contrast to 2-amino-1-metalla-1,3,5-trienes **7** and **11**, which are cyclized thermally to give cyclopentadienes in smooth reaction (Schemes 3 and 4), 2-ethoxy-1-metalla-1,3,5-hexatrienes exhibit a high tendency to undergo cyclization reactions involving nucleophilic attack at the carbene carbon atom.



SCHEME 5. Cyclization of 2-ethoxy-1-metalla-1,3,5-trienes to homopyrroles.

a. *Homopyrroles via (noncatalyzed) cyclization of 2-ethoxy-1-metalla-1,3,5-trienes.* Thermolysis of 2-ethoxy-1-metalla-1,3,5-trienes **5** ($M = \text{Cr}, \text{W}$) leads to production of 2,3-homopyrroles **13** in high yields (88–93%; $R = \text{Ph}, \text{C}_6\text{H}_4\text{Me}, \text{C}_6\text{H}_4\text{OMe}, \text{Me}, i\text{-Pr}, n\text{-Bu}$). This striking difference in reactivity quite obviously rests on the fact that the carbene carbon atom of an alkoxy-carbene compound in general is more susceptible to electrophilic attack than that of an aminocarbene compound. Thus, the cyclization of an 2-ethoxy-1-metalla-triene **5** to an iminium ylide **C** and the subsequent (noncatalyzed) 1,5 hydrogen shift to an intermediate **D** becomes a faster process than cyclization of the 1-metalla-1,3,5-triene unit of **5** with formation of a cyclopentadiene. Homopyrroles **13** are finally obtained from **C** via a (noncatalyzed) 1,5 hydrogen shift to give a species **D**, which has a configuration highly suited for generation of a cyclopropane ring by elimination of the metal moiety (Scheme 5).^{50b}

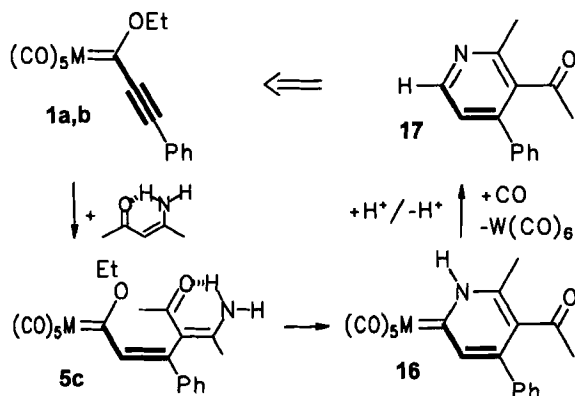
b. *Pyran-2-ylidene and 1,2-dihydropyridin-2-ylidene complexes via base-catalyzed cyclization of 2-ethoxy-1-metalla-1,3,5-trienes.* Cyclization of 2-ethoxy-1-metalla-trienes **5** may afford different products, depending on the reaction conditions. Thus, although cyclization of compounds **5** in the absence of a base catalyst yields homopyrroles **13** (Scheme 5), compounds **5** form pyran-2-ylidene **14** and 1,2-dihydropyridin-2-ylidene **15** complexes⁵⁰ as the only products, if a base is added to the reaction mixture (Scheme 6). This striking change in the reaction course is easily explained. Because 1,6-elimination of ethanol from intermediates **E** and **C** requires base catalysis (for orbital symmetry reasons), this process is retarded in the absence of a base, but it apparently becomes strongly favored over the noncatalyzed 1,5 hydrogen shift in the presence of a base.



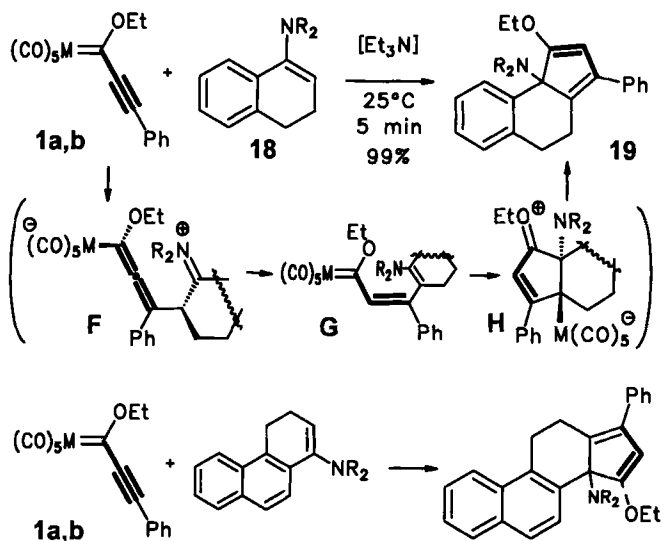
SCHEME 6. Base-catalyzed cyclization of 1-metallatrienes to pyranylidene and dihydropyridinylidene complexes.

c. *Pyridines via fragmentation of 2-ethoxy-1-metalla-1,3,5-trienes.* Formation of pyridines **17** by cyclization of 2-ethoxy-1-metalla-1,3,5-trienes **5** is achieved in two steps by addition of an (NH_2)-enaminone to a (1-alkynyl)carbene complex **1a,b** and subsequent protolysis of the resulting dihydropyridin-2-ylidene complex **16** (Scheme 7).^{50a}

d. *Cyclopentadiene annulation to enamines.* The reactions depicted in Scheme 6 involve a hydrogen migration from the nitrogen atom of the enamino group of compound **5** to a carbon atom. Conceivably, reactions of tertiary instead of secondary enamines with alkynylcarbene complexes **1** must lead to different type products. Tertiary cycloalkenyl amines, e.g., compound **18**, were found to produce 1-metalla-1,3,5-hexatrienes **G** that cyclize spontaneously to cyclopentadienes, e.g., compound **19**, in an overall [C_3+C_2] annulation of carbon templates.⁵⁶ Based on the isolobal relation-



SCHEME 7. Pyridines via dihydropyridinylidene complexes by protolytic ring disengagement.

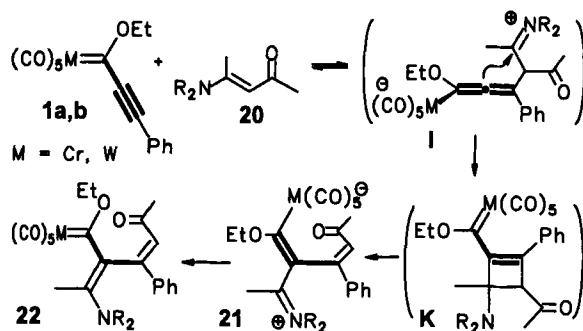


SCHEME 8. Cyclopentadiene annulation of enamines.

ship^{53,54} between $(\text{CO})_5\text{M}=\text{C}$ and $\text{O}=\text{C}$ moieties, reactions of (1-alkynyl) carbene complexes **1** are often compared with those of propargylic esters.⁵² It should be pointed out that the cyclopentadiene annulation to enamines is in marked contrast to the reaction of simple propargylic esters [as compared to (1-alkynyl)carbene complexes] with similar cyclic enamines, in which case seven-membered ring products, resulting from [2+2] cycloaddition followed by ring opening, are isolated. Importantly, all of the steps depicted in Scheme 8 are based upon structures of species analogous to previously isolated and fully characterized compounds (**F**,⁵⁵ **G**,^{48,50a,50b} **H**^{12d}), or they were observed directly.^{56b} The annulation was found to proceed readily with a variety of cyclic five-, six-, and seven-membered ring tertiary enamines. Also, steroid-like ring systems are readily available. The resultant cyclopentadiene products were shown to be produced in good yields, most often at ambient temperature, and in an entirely regiospecific manner (Scheme 8).⁵⁶

4. Cross-Conjugated Metallatrienes

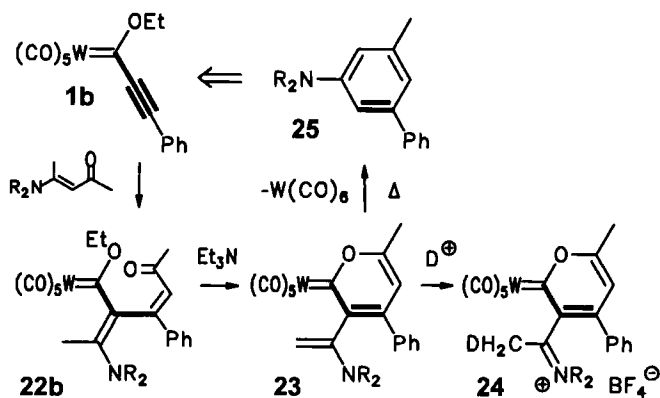
Other than 1-metalla-1,3,5-trienes $\text{M}=\text{C}=\text{C}=\text{C}=\text{C}$, cross-conjugated metallatrienes $\text{M}=\text{C}-\text{C}(=\text{C})-\text{C}=\text{C}$ do not contain a conjugated 6π system. There are several ways to generate such compounds, one of which involves metathesis of a $\text{C}=\text{C}$ bond of an electron-rich alkene at the $\text{C}\equiv\text{C}$ bond of a (1-alkynyl)carbene complex.



SCHEME 9. Cross-conjugated metallatrienes by metathesis of tertiary enamines.

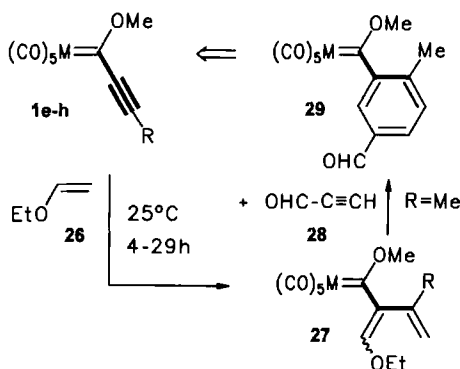
a. *Cross-conjugated metallatrienes by metathesis of enamines.* When open-chain (instead of cyclic) tertiary enamin-3-ones **20** or other open-chain tertiary enamines are reacted with (1-alkynyl)carbene complexes **1a,b** in the absence of base, iminium ylides complexes **21** and/or cross-conjugated metallatrienes (= 2-butadienyl carbene complexes) **22** resulting from a formal metathesis reaction of the $\text{C}=\text{C}(\text{N})$ bond at the $\text{C}\equiv\text{C}$ bond are obtained.^{50c,57} Compounds **21** and **22**, though structurally related, are unambiguously distinguished by ^{13}C NMR chemical shifts as well as by X-ray data. The latter indicate that the $\text{M}^--\text{C}=\text{C}-\text{C}=\text{N}^+$ backbone of compounds **21** is strongly twisted, whereas the $\text{M}=\text{C}-\text{C}=\text{C}-\text{N}$ unit of **22** is essentially planar. It is suggested that metathesis of tertiary enaminones **20** would proceed through formation of a zwitterionic intermediate **I** from which a cyclobutene derivative **K** is obtained, which is considered to be a precursor to **21**. Formation of an intermediate **K** [over a 1,3 hydrogen transfer from the α -carbon atom to the central carbon atom of the allene unit (Scheme 2), resulting in formation of a (conjugated) 1-metalla-1,3,5-hexatriene] seems to be favored by conformational effects (Scheme 9).

b. *Pyranylidene complexes by metathesis of tertiary enamines, and aniline derivatives by fragmentation of pyranilydene complexes.* Addition of a base to cross-conjugated metallatrienes **22b** affords 3-alkenyl pyranilydene complexes **23** by ring closure under (base-induced) 1,4-elimination of ethanol. For related reactions, see Schemes 22 and 24. Compounds **23** form (stable) iminium derivatives **24** on addition of $\text{D}[\text{BF}_4]$. They undergo a thermal fragmentation by elimination of $\text{W}(\text{CO})_6$ ("retro-Fischer reaction") to give a 1,3,5-substituted aniline **25** (Scheme 10).^{50c} Note that during the reaction leading to formation of compound **25**, the connectivity of the carbon skeleton of the enaminone undergoes a drastic change.



SCHEME 10. Pyranylidene complexes by metathesis of tertiary enaminones.

c. *Cross-conjugated metallatrienes by metathesis of enols.* Metathesis of a C=C bond of an electron-rich alkene at the C≡C bond of a (1-alkynyl)carbene complex can be achieved under certain circumstances with enamines as well as with enol ethers. Thus, reaction of the open-chain enol ether **26** with a (1-alkynyl)carbene complex **1e-h** ($\text{M} = \text{Cr}$, W ; $\text{R} = \text{Me}$, SiMe_3 ; 32–56%) yields cross-conjugated metallatrienes **27** (Scheme 11). Few reactions of cross-conjugated metallatrienes have been reported thus far. They include ring closure (Scheme 10) and the [4+2] cycloaddition of the electron-deficient alkyne **28** to compound **27b** ($\text{M} = \text{W}$) with subsequent 1,2-elimination of ethanol to give an arylcarbene complex **29**.⁵⁸



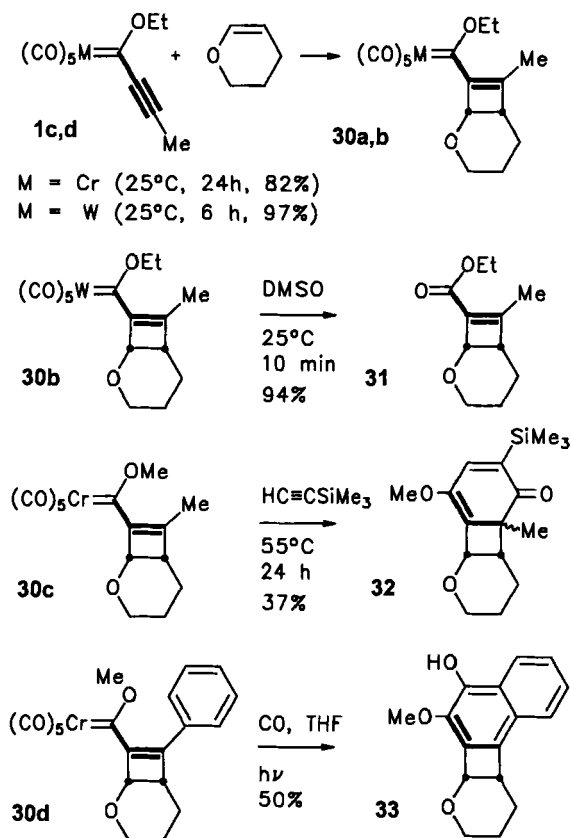
SCHEME 11. Aryl derivatives by [2+1+1+2] cycloaddition.

C. Cycloaddition Reactions of Enol Ethers and of Dienes to the $C\equiv C$ Bond

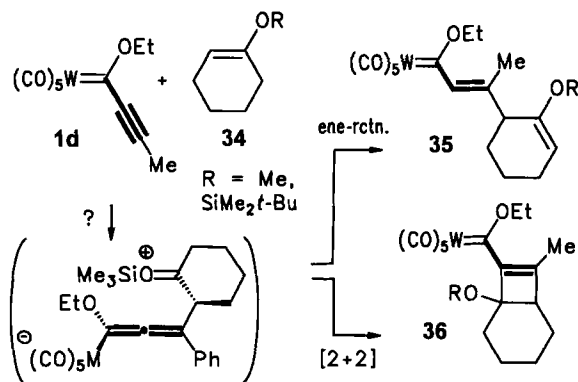
Many cycloaddition reactions to the $C\equiv C$ bond of (1-alkynyl)carbene complexes have been reported.

1. Cyclobutene Derivatives by [2+2] Addition of Enol Ethers and Silyl Enol Ethers

(1-Alkynyl)carbene complexes **1c,d** form cyclobutene derivatives **30a,b** by [2+2] cycloaddition of a cyclic enol ether under mild conditions (Scheme 12).⁵⁸ The cycloaddition was found to be sensitive toward pressure and showed a remarkable rate acceleration independent of the metal center, consistent with a nonpolar, concerted, synchronous one-step mechanism.⁵⁹



SCHEME 12. Cyclobutene derivatives by [2+2] cycloaddition.



SCHEME 13. [2+2] addition vs. ene reaction.

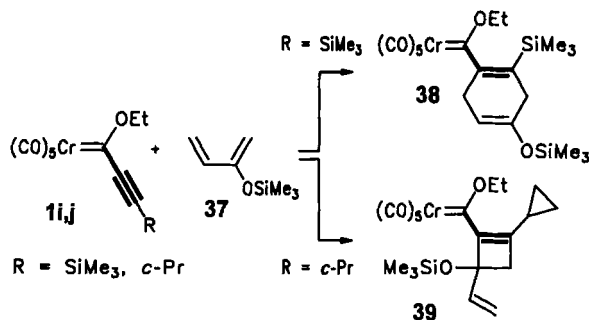
Examples of transformations of a cyclobutene compound **30** into organic products include formation of an ester **31** by oxidation of **30b** with DMSO,⁵⁸ formation of a cyclohexadienone **32** by reaction of **30c** with an alkyne,^{58,60} and formation of a naphthole **33** by photolysis of the phenyl derivative **30d** (Scheme 12).⁶¹

2. Formation of "Ene" Products

Enol ethers of type **34a** (R = Me), as well as silyl enol ethers **34b** [= SiMe₂(*t*-Bu)], may produce cyclobutene derivatives **36a,b** together with open-chain adducts **35a,b** (Scheme 13),^{62,63} in a product ratio **35**:**36**, which strongly depends on the nature of the substituent R = Me (**35**:**36** = 23:77) and SiMe₂(*t*-Bu) (90:10).^{63,3d}

3. [4+2] versus [2+2] Cycloadditions

(1-Alkynyl)carbene complexes (CO)₅M=C(OR)–C≡CR¹ (M = Cr, W; R¹ = *n*-Pr, Ph, SiMe₃) as well as tetraalkoxyethylenes (RO)₂C=C(OR)₂ (R = Me, Et) give [2+2] adducts in 65–82% yield, from which cyclobutene carboxylates have been obtained by oxidative decomposition with DMSO.⁶⁴ Diethoxy acrylates (EtO)₂C=CHCO₂R (R = Me, Et) afford mixtures of several products, that is, pyranilidene complexes and cross-conjugated metallatrienes.⁶⁵ Trimethylsiloxy butadiene **37** forms [4+2] as well as [2+2] adducts, depending on the substituent R of the (1-alkynyl)carbene complex **1i,j**. Thus a Diels–Alder product **38** is obtained from the trimethylsilyl



SCHEME 14. [4+2]- vs [2+2] cycloaddition.

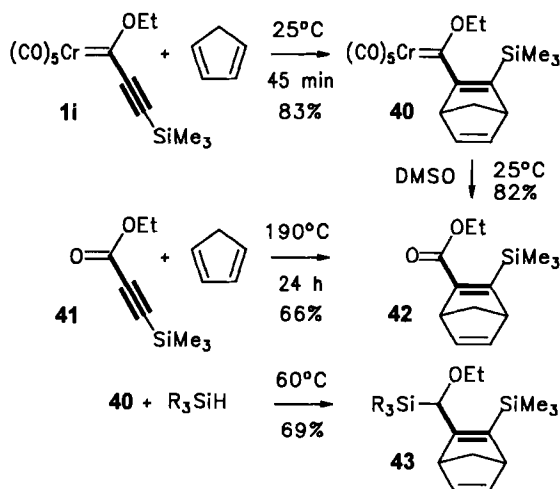
derivative **1i**,⁶⁶ but a [2+2] adduct **39** of the C=C bond substituted by the siloxy group is generated with the cyclopropyl derivative **1j** (Scheme 14).⁶⁷

4. Norbornadiene Derivatives by [4+2] Cycloaddition of 1,3-Dienes

Cycloaddition reactions of α,β -unsaturated chromium and tungsten complexes have been studied to a great extent and have been reviewed.^{3c-e} Our report on cycloaddition of (1-alkynyl)carbene complexes is restricted to a short abstract and an update including more recent results. A most remarkable feature of [4+2] cycloadditions of 1,3 dienes to C≡C bonds of (1-alkynyl)carbene complexes, e.g., **1i**, is that such reactions proceed under very mild conditions, compared to those for reactions of propargylic esters, e.g., **41**. Thus, formation of a Diels–Alder adduct, e.g., a norbornadiene derivative **42**, can be achieved at 25°C via carbene complexes instead of at 190°C via the direct route (Scheme 15).⁶⁸ Ligand disengagement from compound **40** can be achieved in various ways, e.g., by formation of an ester **43** through oxidation of the Cr=C bond, or by formation of an allyl silane **43**⁶⁹ or a stannane.^{70,71}

5. Polycyclic Carbon Skeletons by Tandem Cycloaddition/Annulation Reactions

Bi- and tricyclic carbocyclic ring systems can be easily obtained from (1-alkynyl)carbene complexes in two or more reaction steps without isolation of intermediate products. For example, the bicyclic 1,3-dienone **44** has been generated from compound **1e** in a two-step cycloaddition/annulation procedure involving [4+2] cycloaddition of a diene to the C≡C bond of a (1-alkynyl)carbene complex and a subsequent Dötz reaction.⁶⁸ Furthermore, a 1,4-dioxy dihydronaphthalene **45** was obtained from the silyl derivative **1g** in a similar reaction sequence. In contrast to the methyl derivative **44**, the corresponding silyl derivative generated from **1g** undergoes facile



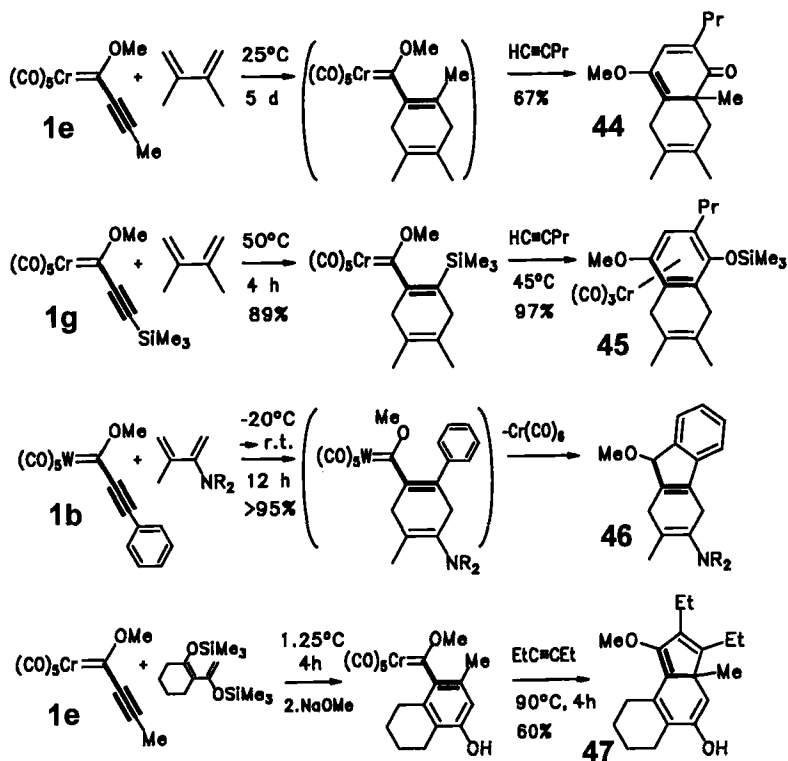
SCHEME 15. [4+2] cycloadditions.

migration of the silyl group from the carbon to the oxygen atom, forming an aromatic ring instead of a 2,4-cyclohexadienone (Scheme 16).^{68,72} Addition of a 2-amino-1,3-diene to the tungsten complex **1b** affords a dihydrofluorene derivative **46**, in which a five-membered ring is formed from the $\text{C}-\text{C}\equiv\text{C}$ unit of the (1-alkynyl)carbene ligand without insertion of carbon monoxide.⁷³ A cyclopentadiene annulation with formation of an angularly fused tricyclic product **47** from the Diels–Alder adduct of a disiloxy vinylcyclohexene to compound **1e** was obtained in 60% yield.⁷⁴ The principles outlined in Scheme 16 also have been applied for the synthesis of precursors of anthracyclinones.⁶⁶

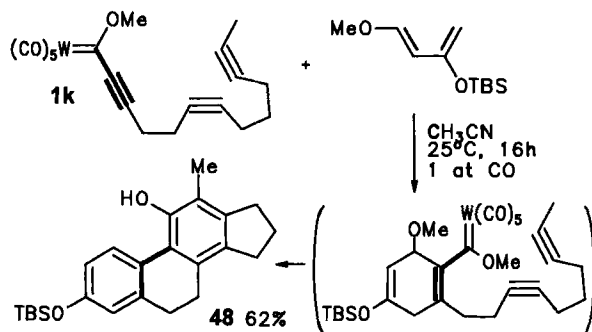
Steroid-type molecules, e.g., **48**, were generated from (1-alkynyl)carbene complex **1l** by [4+2] cycloaddition of a TBSO butadiene to the C2–C3 triple bond of **1k** and subsequent two-alkyne annulation to the $\text{M}=\text{C}$ bond (Scheme 17).⁷⁵ Other polycyclic compounds have been obtained similarly by insertion of several alkyne units tethered by a carbon chain.^{76,77} It should be noted that an annulation of an aromatic ring instead of a 1,4-cyclohexadiene is achieved if the diene component contains a potential leaving group, as shown in Schemes 16 and 17.

D. Cyclization Reactions

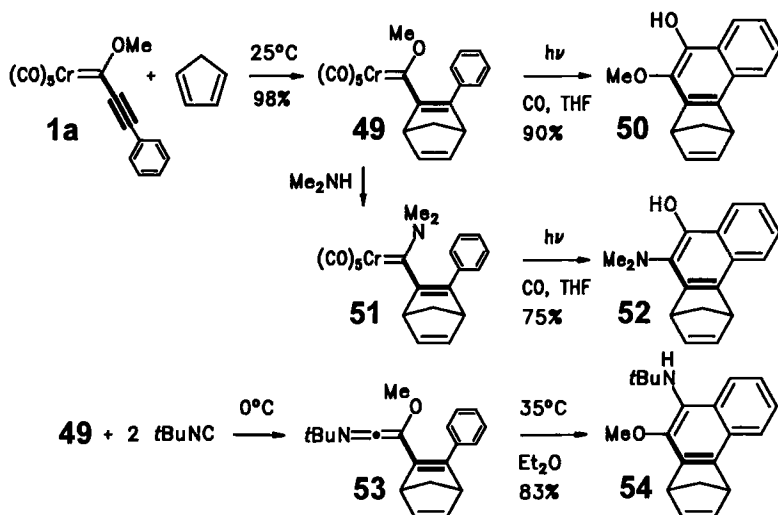
Cycloadducts to the $\text{C}\equiv\text{C}$ bond of (1-alkynyl)carbene complexes can be transformed into organic products, e.g., by various subsequent cyclization reactions.



SCHEME 16. Tandem cycloaddition/annulation.



SCHEME 17. Steroid-type molecules by two-alkyne annulation.



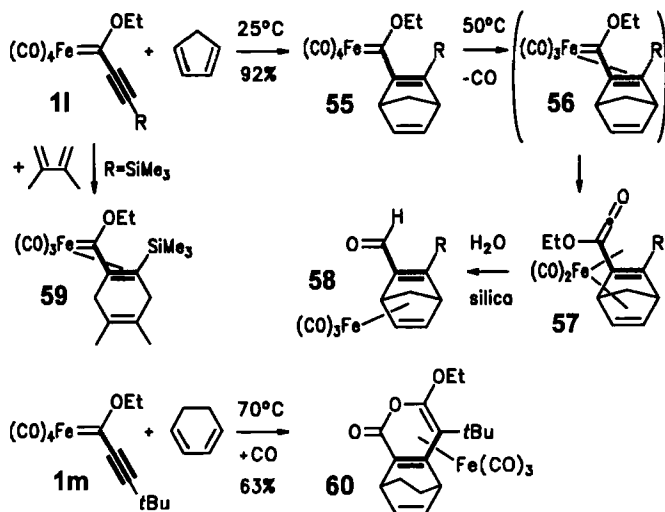
SCHEME 18. 1,2-Dioxy-, 2-amino-1-oxy, and 1-amino-2-oxy cyclization.

1. 1,2-Dioxy- and 2-Amino-1-oxy Photocyclization as well as 1-Amino-2-oxy Cyclization via Ketenimine Complexes

For example, photocyclization^{61,78} of compound **49**, derived from the phenyl complex **1a** by addition of cyclopentadiene, was shown to afford the 1,2-dioxy naphthalene **50** (Scheme 18).⁷⁹ Thus, the regiochemistry of this type of ring annulation is complementary to that of the Dötz reaction, which yields 1,4-dioxy compounds. Photocyclization of aminocarbene complex **51**⁸⁰ involves insertion of carbon monoxide and leads to production of an 2-amino-1-oxy naphthalene derivative **52**. Regio isomers, e.g., 1-amino-2-oxy compounds **54**, can be generated thermally by intermediate formation of a ketene imine **53** by addition of an isocyanide to compound **49**.^{79,81,82} (Amino)alkynylcarbene complexes also give [4+2] cycloadducts, but they prove to be much less reactive than the corresponding alkoxy-carbene compounds (Scheme 18).^{42,83}

2. Pyrones via Iron Complexes

The chemistry of (1-alkynyl)carbene iron complexes is different from that of chromium and tungsten compounds. [4+2] cycloaddition of cyclopentadiene to a (1-alkynyl)carbene iron complex **11,m** ($\text{R} = \text{SiMe}_3$, *t*-Bu, *c*- C_6H_{11} , *n*-Pr, Ph) affords (1-alkenyl)carbene $\text{Fe}(\text{CO})_4$ complexes **55**, but these are readily isomerized at 50°C to $\text{Fe}(\text{CO})_2$ complexes **57** by insertion of carbon monoxide into the $\text{Fe}=\text{C}$ bond of an intermediate $\text{Fe}(\text{CO})_3$

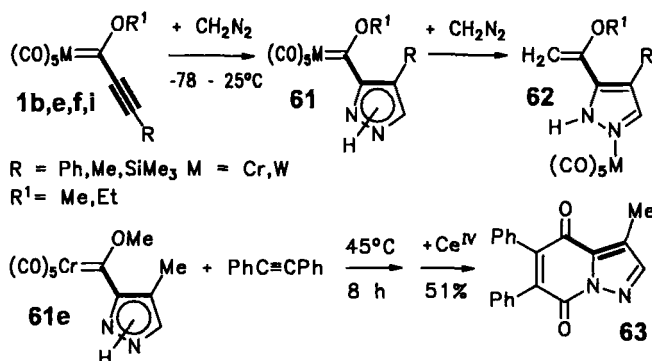


SCHEME 19. [4+2] cycloadditions of iron complexes.

complex. Compounds **57** form aldehydes on chromatography on silica gel.⁸⁴ In contrast to the Fe(CO)₃ compounds **56**, which have not been isolated, the silyl complex **59** could be characterized by X-ray analysis.^{30,33} Although addition of 1,3-cyclohexadiene to complex **1I** (R = SiMe₃) affords products analogous to those obtained with cyclopentadiene, addition of 1,3-cyclohexadiene to the corresponding *t*-butyl derivative **1m** yields an α -pyrone complex **60** by subsequent insertion of 2 eq CO (Scheme 19).⁸⁵ [4+2] cycloadditions to the C \equiv C bond of cationic amino(1-alkynyl)carbene iron complexes have been also reported.^{38c}

E. Cycloaddition Reactions of 1,3-Dipoles to the C \equiv C Bond

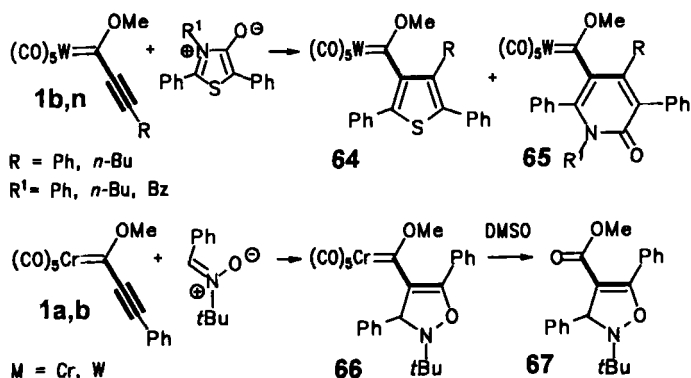
1,3-Dipolar cycloaddition reactions are most commonly applied for the synthesis of five-membered heterocyclic compounds.^{86,87} [3+2] cycloaddition reactions of transition-metal propargyl complexes have been reviewed.⁸⁸ Addition of diazomethane to carbene complexes (CO)₅Cr=C(OEt)R results in cleavage of the M=C bond with formation of enol ethers H₂C=C(OEt)R,^{3,89} but (1-alkynyl)carbene complexes undergo 1,3-dipolar cycloaddition reactions at the M=C as well as at the C \equiv C bond. Compound **1b** (M = W, R = Ph) affords a mixture of pyrazole derivatives **61** and **62** with 1 eq diazomethane,⁹⁰ but compound **62** is obtained as sole



SCHEME 20. [3 + 2]cycloaddition of diazomethane.

product if an excess of diazomethane is applied (Scheme 20).⁹¹ Selective formation of **61e** was achieved from (1-alkynyl)carbene complex **1h** (M = W, R = SiMe₃, R' = Et).⁹² Addition of trimethylsilyl diazomethane affords pyrazoles in good to excellent yields.⁹³ (1-Alkenyl)carbene complexes react similarly to (1-alkynyl)carbene complexes **1**.^{94,95} Benzannulation reaction of the pyrazole chromium complex **61e** with diphenylacetylene followed by an oxidative workup gave the pyrazolo pyridine quinone **63** (Scheme 20).⁹⁶ Notably, in this cyclization only the C,N unsaturation was involved in the benzannulation reaction, whereas products from incorporation of the C,C unsaturation were not observed.

Addition of 1,3-thiazolium-4-olates to (1-alkynyl)carbene tungsten complexes **1b,n** affords thiophene and/or pyridone complexes, **64** and **65**, by extrusion of sulfur and isocyanate, respectively, from the [3+2] adduct formed initially (Scheme 21).⁹⁷ [3+2] cycloaddition reactions of azomethine



SCHEME 21. [3+2] cycloaddition of thiazolium olates and nitrones.

imines and azimine ylides also have been studied.⁹⁸ Addition of an *N*-alkyl nitron yields a Δ^4 -(isoxazoliny)carbene complex **66**,⁹⁹ from which the ester **67** has been obtained by oxidation with DMSO. *N*-Aryl nitrones were shown to give (oxazoliny)carbene complexes⁹² by rearrangement.¹⁰⁰ Attempted addition of azides to (1-alkynyl)carbene complexes leads to (2-amino) alkenyl carbene complexes.¹⁰¹

F. Pyranlydene Complexes

Pyranlydene complexes, which are easily obtained from (1-alkynyl)carbene complexes, prove to be most valuable building blocks for the generation of open-chain 1-metalla-1,3,5-trienes as well as of cyclohexadiene annulation products.

1. Pyranlydene Complexes by C-Addition of Enolizable Carbonyl Compounds

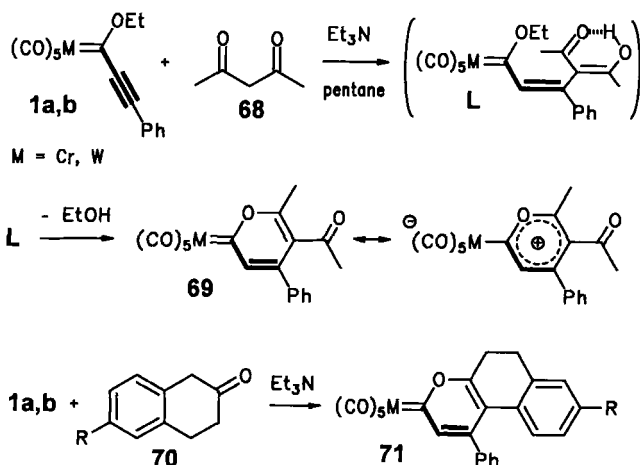
Addition of carbon nucleophiles to the $C\equiv C$ bond of a compound **1a,b** includes reactions of enolizable carbonyl compounds, enol ethers, and enamines, as well as lithium alkyls and zinc alkyls. Condensation of the enolizable ketone **68** with **1a,b** ($M = Cr, W$)²⁶ is induced, for example, by catalytic amounts of triethylamine in pentane and *under these conditions* affords a 90% yield of crystalline pyranlydene complex **57** directly from the reaction mixture.¹⁰² This reaction proceeds via the 2-ethoxy-1-metallatriene **L**, which, because of the presence of triethylamine, rapidly undergoes ring closure to the pyranlydene (pyrylium ylide) complex **69** by 1,6-elimination of ethanol (Scheme 22). Chromanylydene complexes **71** are obtained from condensation of a β -tetralone **70** ($R = H, OMe$) with compound **1a,b**.

2. Divinyl Enol Ether Carbene Complexes (= 4-Enoxy-1-metalla-1,3-dienes) by O-Addition of Enols

Addition of enolizable carbonyl compounds to the $C\equiv C$ bond of (1-alkynyl)carbene complexes can proceed by *C*- or *O*-addition of the enol unit. The *C/O* ratio depends very much on the substrate as well as on the reaction conditions. Reaction of cyclic 1,3-diketones **72** in diethyl ether in the presence of catalytic amounts of Et_3N results in the formation predominantly of (red) divinyl ethers **73** (by *O*-alkylation) together with smaller amounts of (blue) pyranlydene complexes **74** by (*C*-alkylation) (Scheme 23).^{26,103} For related reactions, see Scheme 67.

3. Amino-1-metalla-1,3,5-trienes via Pyranlydene Complexes

Aminolysis of pyranlydene complex **69b** with primary amines RNH_2 ($R = n\text{-Bu}, i\text{-Pr}, CH_2Ph, \text{allyl}$) gives easy access to the formation of amino

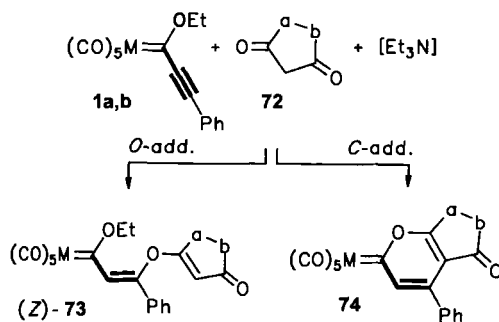


SCHEME 22. C-addition of enolizable carbonyl compounds.

1-metalla-1,3,5-trienes **75** and/or **76**.¹⁰² Compounds **75** are generated in a fast and reversible addition, whereas compounds (*Z*)-**76** are formed in a slow and irreversible ring-opening reaction. The latter compounds undergo a slow configurational change to give the isomers (*E*)-**76** (Scheme 24).

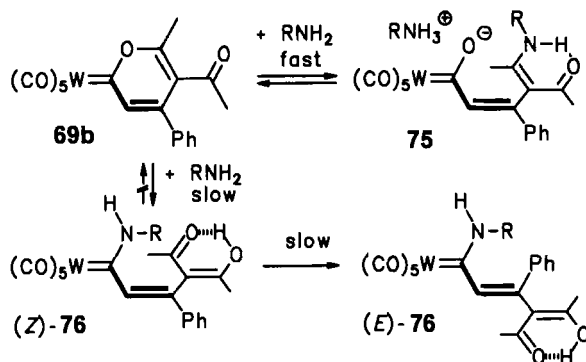
4. 2-Amino-1-metalla-1,3,5,7-octatetraenes via 6-Alkenyl Pyranilydene Complexes

2-Amino-1-metalla-1,3,5,7-octatetraenes **77** ($\text{M} = \text{Cr}, \text{W}$) are obtained in two steps involving base-catalyzed addition of a 1-hexen-3,5-dione to (1-alkynyl)carbene complexes **1a,b** ($\text{M} = \text{Cr}, \text{W}$) to give styryl pyranilydene



$\text{M} = \text{Cr}, \text{W}$; $\text{a-b} = \text{CH}_2\text{CH}_2, \text{CH}_2\text{CMe}_2\text{CH}_2$

SCHEME 23. C- vs O-addition of 1,3 diketones.

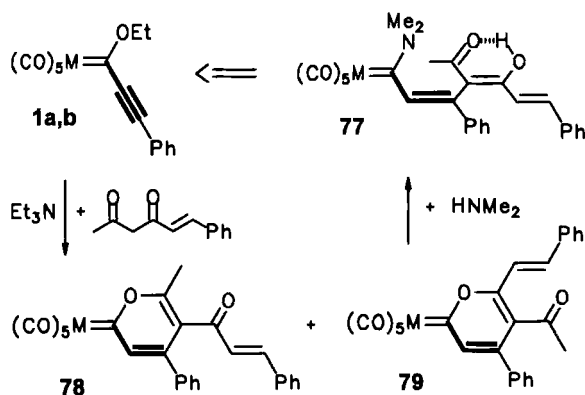


SCHEME 24. Amino 1-metalla-1,3,5-hexatrienes via pyranilydene complexes.

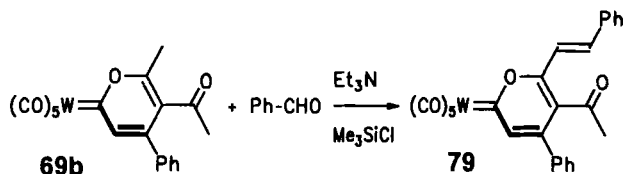
complexes **78** and **79**, both of which afford compounds **77** on aminolysis with HNMe_2 (Scheme 25).¹⁰⁴

5. Condensation of Pyranilydene Complexes with Aldehydes

The 6-methyl group of the pyranilydene complex **69b** is even more acidic than the acetyl group and readily undergoes base-catalyzed H/D exchange reactions as well as condensation reactions with aldehydes. Thus, a route to styryl pyranilydene complexes **79** other than that shown in Scheme 25



SCHEME 25. 2-Amino-1-metalla-1,3,5,7-octatetraenes.



SCHEME 26. Condensation of pyranylidene complexes with aldehydes.

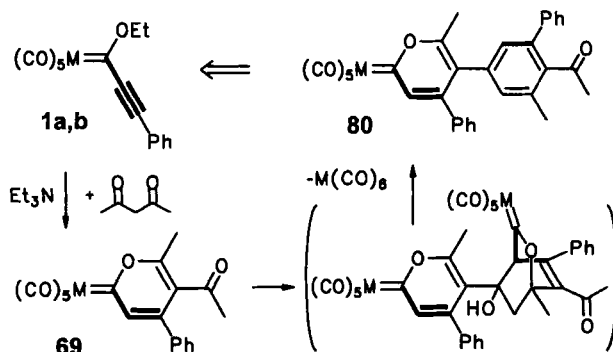
involves condensation of pyranylidene complex **69b** with benzaldehyde in the presence of $\text{Et}_3\text{N}/\text{SiMe}_3\text{Cl}$ (Scheme 26).

6. Self-Condensation of Pyranylidene Complexes

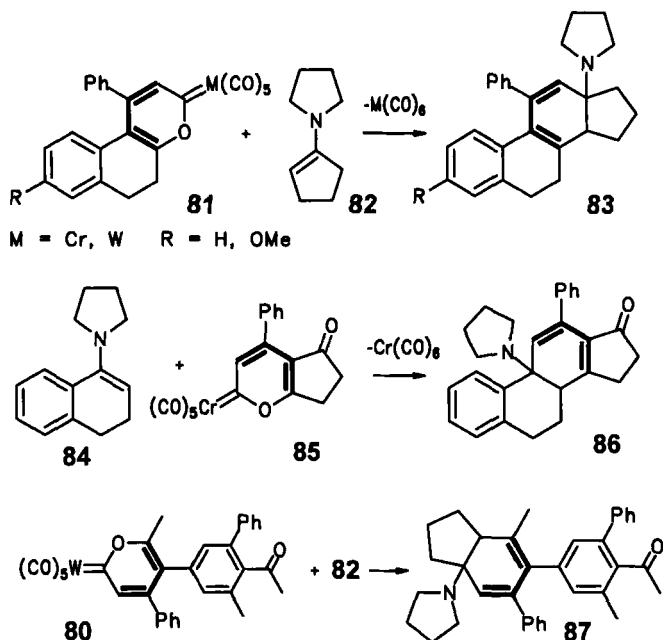
5-Acetyl pyran-2-ylidene complexes **69a,b** ($\text{M} = \text{Cr}, \text{W}$) are generated in the presence of base, but they undergo self-condensation under these conditions and form (cherry-red) biphenyl derivatives **80a,b** by extrusion of $\text{M}(\text{CO})_6$ (Scheme 27). Compounds **80a,b** are obtained in yields up to 82–85% if pyran-2-ylidene complexes **69** are treated, for example, with Et_3N in acetone as solvent (Scheme 27).¹⁰⁵

7. Cyclohexadiene Annulation to Enamines via Pyranylidene Complexes

“Enaminolysis” of pyranylidene complexes affords cyclohexadiene annulation products.²⁶ For example, steroid-like molecules **83** are obtained most straightforwardly by this route if the chromanylidene complex **81** is added to the enamine **82**. The annulation is highly regioselective, exemplified by the formation of compound **86** from chromanylidene complex **85** and enamine **84**, and also by the straightforward generation of the sterically



SCHEME 27. Self-condensation of pyranylidene complexes.



SCHEME 28. Cyclohexadiene annulation to enamines.

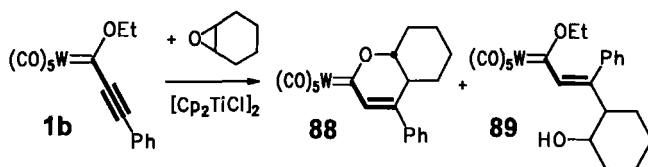
congested compound **87** from the readily available precursor **80** (Scheme 28).¹⁰⁵

G. Radical Addition

To date, few radical reactions with Fischer carbene complexes have been reported. Alkyl and acyl radicals could be generated from (1-acyl)carbene complexes,¹⁰⁶ and it has been shown, for example, that radicals are involved in the tungsten catalyzed polymerization of terminal alkynes.¹⁰⁷ Alkyl radicals generated by reaction of titanocene monochloride dimer with epoxides have been added stoichiometrically to (1-alkynyl)carbene tungsten complexes **1b** to afford a 36:20% mixture of the dihydropyranylidene complex **88**, containing a *trans*-fused ring junction, together with the alcohol **89** (Scheme 29).¹⁰⁸

H. Cyclopentenylidene Complexes by Base-Induced [3+2] Dimerization of the Ligand

Addition of aryl lithium compounds to a (1-alkynyl)carbene complex **1a,b** affords Michael adducts **90** in up to 45% yield, together with cyclopenten-

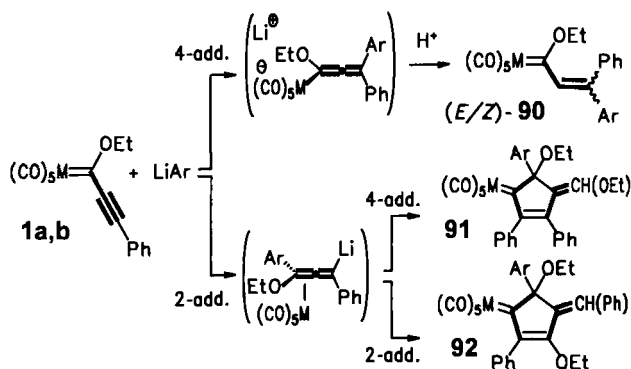


SCHEME 29. Addition of epoxides.

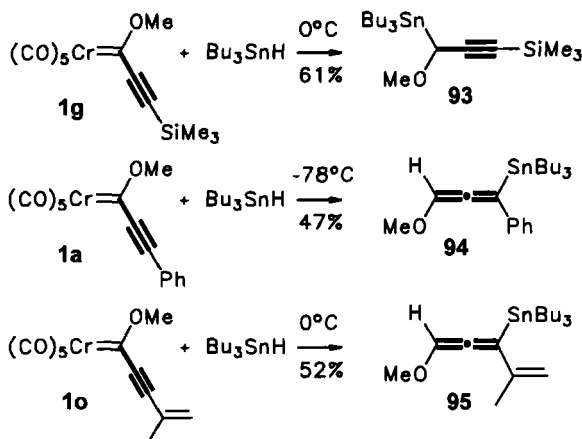
tenylidene complexes **91** and **92** in a ratio depending on the reaction temperature (Scheme 30).¹⁰⁹ Addition of Et_2Zn to **1a,b** affords products of the latter type only.¹¹⁰

I. Ligand Disengagement by Hydrostannation

Hydrostannation of (1-alkynyl)carbene chromium complexes involves addition to the $\text{M}=\text{C}$ bond as well as to the $\text{C}\equiv\text{C}$ bond and is strongly influenced by the substituent at the alkynyl moiety. By the bulky trimethylsilyl group of compound **1g**, a 1,1-addition to the carbene carbon atom is promoted with formation of a densely functionalized 1,3-heterobimetallic propargyl reagent **93** containing both a stannyl and a silyl group. A 3,1-addition is observed with phenyl derivative **1a** and also the vinyl compound **1o**, which leads to production of an allene **94** and **95**, respectively (Scheme 31).¹¹¹



SCHEME 30. Dimerization by addition of lithium aryls.



SCHEME 31. 1- and 3-addition of tin hydrides.

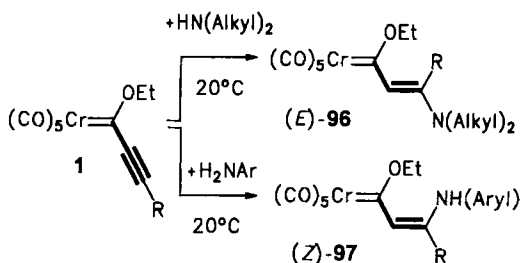
IV

REACTION WITH NITROGEN AND PHOSPHORUS NUCLEOPHILES

Reaction of (1-alkynyl)carbene complexes with nitrogen- or phosphorus-containing compounds makes available a large variety of products. Among these are (enamino)carbene and ("enphosphino")carbene complexes, both of which have been widely used for the generation of organic products.

A. 4-Amino-1-chroma-1,3-dienes, 2-Amino-1-metalla-1-en-3-yne, and 4-Amino-1-metalla-1,2,3-butatrienes by Aminolysis

Aminolysis of (1-alkynyl)carbene complexes may involve addition to the $\text{M}=\text{C}$ as well as to the $\text{C}\equiv\text{C}$ bond, which leads to different products. Nevertheless, such reactions also can be so selective that under appropriate conditions a single product is obtained. Thus, addition of a *secondary* alkyl amine $\text{HN}(\text{alkyl})_2$ (e.g., dimethylamine or morpholine) to a chromium compound **1** ($\text{R}^1 = \text{Ph}, \text{Me}, t\text{-Bu}, n\text{-Pr}, i\text{-Pr}, c\text{-Pr}$) at 20°C produces 4-amino-1-chroma-1,3-dienes **96** in virtually quantitative yield. In most cases, except when R^1 on the alkynyl terminus is extremely bulky, compounds **96** have an (*E*)-configured $\text{C}=\text{C}(\text{N})$ bond (Scheme 32). Furthermore, addition of *primary aryl* amines H_2NAr to compounds **1** is highly regio- and stereoselective and yields complexes **97** in the (*Z*)-configuration only.²¹ Some examples of 4-amino-1-chroma-1,3-dienes as well as typical spectroscopic data are given in Table IV. It should be noted that the ^{13}C NMR chemical shift



SCHEME 32. Formation of 4-amino-1-chroma-1,3-dienes with high regio- and stereoselectivity.

of the carbene carbon atom of compounds $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{CR}(\text{NR}^1\text{R}^2)$ clearly reflects the π -electron-donor propensity of the amino function, indicating the stronger contribution of an iminium ylide structure $^-(\text{CO})_5\text{M}-\text{C}(\text{OEt})=\text{CH}-\text{CR}(=\text{N}^+\text{R}^1\text{R}^2)$ by an upfield shift in the case

TABLE IV
 ^{13}C NMR SHIFTS (δ VALUES, CDCl_3) AND IR FREQUENCIES (cm^{-1}) OF SELECTED
 ALKOXY(2-AMINOALKENYL)CARBENE (= 4-AMINO-1-CHROMA-1,3-DIENES) AND ALKOXY(2-
 PHOSPHINO)CARBENE COMPLEXES (= 4-PHOSPHINO-1-CHROMA-1,3-DIENES)
 $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{CH}=\text{CR}(\text{ER}^1\text{R}^2)$

M	E	R	R ¹	R ²	Cfg ^a	S ^b	$\delta(\text{C1})$	$\delta(\text{C2})$	$\delta(\text{C3})$	$\nu(\text{C}\equiv\text{O})^c$	Ref.
Cr	N	Ph	Me	Me	<i>E</i>	^d	293.7	118.8	156.2	2048, 1982, 1928	21
Cr	N	<i>c</i> -Pr	pyrrolidine		<i>E</i>	^d	290.9	118.7	152.7	2047, 1981, 1928	20
Cr	N	Ph	H	Ph	<i>Z</i>	^e	290.7	119.3	155.9	2050, 1937, 1931	21
Cr	N	Ph	PhCO	Ph	<i>Z</i>	^d	330.1	135.1	141.9	2056, 1985, 1947	120
Cr	P	Ph	Cy	Cy	<i>E</i>	^d	336.7	146.1	143.4	2056, 1984, 1943	55b
W	N	Ph	H	Ph	<i>Z</i>	^e	268.9	122.0	159.2	2059, 1935, 1927	21
W	N	Ph	PhCO	Ph	<i>Z</i>	^d	304.2	138.9	141.0	2065, 1982, 1943	120
W	P	Ph	Cy	Cy	<i>E</i>	^d	309.3	149.7	147.2	2064, 1974, 1941	55b

^a Configuration.

^b Solvent of ^{13}C NMR spectrum.

^c In hexane.

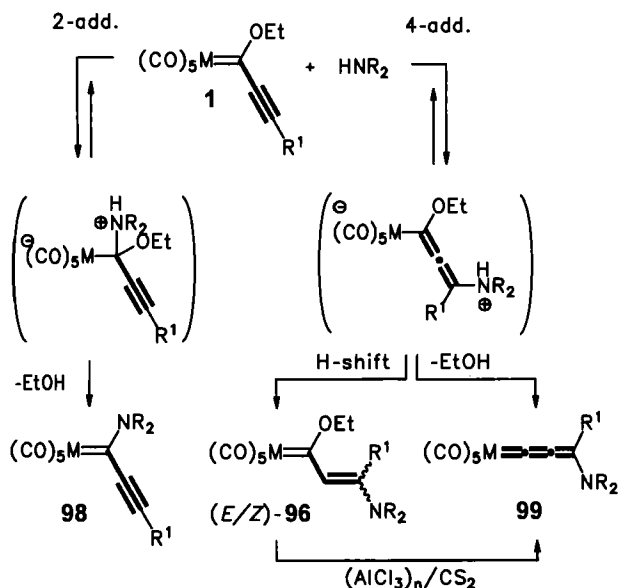
^d In C_6D_6 .

^e In CDCl_3 .

of *N*-alkyl or *N*-aryl substituents compared to spectra of *N*-acyl substituents. The iminium ylide structure of 4-amino-1-metalla-1,3-dienes also is supported by several X-ray structure analyses.^{23,117,119}

The observation by Fischer *et al.*¹⁸ that the 4,1-addition of dimethylamine to compound **1a** is thermodynamically controlled at 20°C, whereas 2,1-addition/elimination is kinetically controlled at -115°C, turned out to be limited to few cases.²⁰ It has been shown^{9a,9b,42,112,113} that for most cases, three competing reaction paths must be considered: (i) 2,1-addition/elimination with formation of (1-amino)alkynylcarbene complexes (= 2-amino-1-metalla-1-en-3-yne) **98**; (ii) 4,1-addition to give [(2-amino)alkenyl]carbene complexes (= 4-amino-1-metalla-1,3-butadienes) **96**; and (iii) 4,1-addition/elimination to (3-amino)allenylidene complexes (= 4-amino-1-metalla-1,2,3-butatrienes) **99** (Scheme 33, M = Cr, W). The product ratio **96**:**98**:**99** depends on the bulk of substituents R and R¹, as well as on the reaction conditions. Addition of lithium amides instead of amines leads to predominant formation of allenylidene complexes **99**.¹¹² Furthermore, compounds **99** also can be generated by elimination of ethanol from complexes **96** with BF₃ or AlEt₃¹¹⁴ and AlCl₃,¹¹³ respectively.

4-Amino-1-chroma-1,2,3-butatrienes **99** are most conveniently distinguished from the corresponding 2-amino-1-chroma-1-buten-3-yne **98**. The former compounds exhibit a strong [$\nu(\text{C}=\text{C}=\text{C})$] band at 1974–1988 cm⁻¹



SCHEME 33. Principal routes of aminolysis of 2-ethoxy(1-alkynyl)carbene complexes.

TABLE V
¹³C NMR SHIFTS (δ VALUES, CDCl₃) AND IR FREQUENCIES (cm⁻¹, HEXANE) OF SELECTED
 (AMINO)ALLENYLIDENE COMPLEXES (CO)₅Cr=C=C=CPh(NR¹R²)

R	R ¹	δ (Cr=C)	δ (C3)	δ (C2)	ν (C \equiv O)	ν (C=C=C)	Ref.
H	Galacto ^a	252.7	147.0	127.8	2076, 1943	1977	116
<i>i</i> -Pr	<i>i</i> -Pr	238.3	152.0	65.8 ^b	2098, 1924	1976 ^c	9a, 9b, 20, 112
Me	Me	230.2	153.1	125.3	2078, 1939	1988	113
Me	Ph	243.6	150.2	129.5	2071, 1943	1978	113
Et	Ph	240.0	150.9	129.3	2075, 1943	1977	113
	IndolinyI	239.0 (243.0)	144.3 (143.9)	125.8 (125.1)	2072, 1940	1974	113

^a 2,3,4,6-Tetra-*O*-pivaloyl- β -D-galactopyranosylamino.

^b δ = 126.7 is quoted in Ref. 115 instead of δ = 65.8 in Ref. 9.

^c In Ref. 9 this band is assigned to ν (C \equiv O) instead of ν (C=C=C).

and a (usually weak) [ν (C \equiv O)] A¹-band at 2071–2098 cm⁻¹, whereas the latter compounds are identified by a [ν (C \equiv C)] band at 2165–2175 cm⁻¹ and a [ν (C \equiv O)] band at 2058–2065 cm⁻¹. Further spectroscopic data are given in Table V. The Cr=C2=C3=C4 backbone of 4-amino-1-chroma-1,2,3-butatrienes **99** is almost linear. Because the bond lengths C2–C3 and C4–N are very short, a zwitterionic (iminium)alkynyl ylide structure ⁻(CO)₅M–C \equiv C–C(=N⁺R₂)R¹ gives a more adequate description of the bond distances than does the allenylidene structure (CO)₅M=C=C=C(NR₂)R¹.^{113,114} For a review of allenylidene complexes, see Ref. 115.

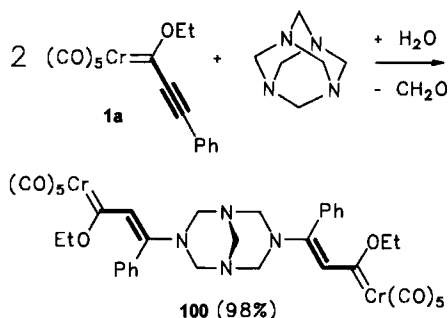
B. Binuclear 4-Amino-1-metalla-1,3-dienes

A binuclear bridged (2-aminoalkenyl)carbene complex **100** (X-ray analysis available) is formed on reaction of compound **1** with urotropin in the presence of water by partial fragmentation of the urotropin skeleton with elimination of formaldehyde (Scheme 34).¹¹⁷

C. Cyclopentadienes via 6-Amino-1-metalla-1,3,5-trienes by [3+2]

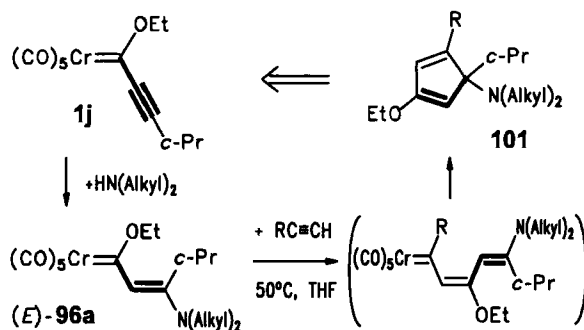
Cycloaddition of a 4-Amino-1-metalla-1,3-diene to an Alkyne
 ("Alkyne Route")

Addition of alkynes to [2-(amino)alkenyl]carbene complexes (*E*)-**96a** does not afford cyclohexadienones (as might have been anticipated in case of a Dötz-type reaction),³ but gives cyclopentadienes **101** instead (Scheme 35).^{3r,9a,9b} It is important to note that the assembly of the cyclopentadiene

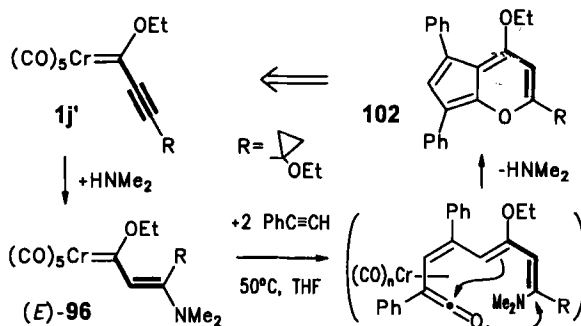


SCHEME 34. Binuclear 4-amino-1-metalla-1,3-dienes.

ring from a C_3 and a C_2 unit by the "alkyne route" follows a regiochemistry different from that of the "enamine route" to cyclopentadienes shown in Schemes 3 and 4. Though both routes proceed through 1-metalla-1,3,5-trienes as precursors to cyclopentadienes, the 1-metalla-1,3,5-trienes exhibit characteristically different substitution patterns with respect to the amino function, which is located at C2 in one case and at C6 in the other, thus inducing a marked difference in reactivity of the 1-metalla-1,3,5-triene system. In the alkyne route it is the C_2 unit that is attached directly to the metal atom, whereas in the enamine route it is the C_3 unit that is arranged next to the metal atom. It has been previously demonstrated that isolable 1-chroma-1,3,5-trienes are obtained by addition of an 1-amino alkyne to a 1-chroma-1,3-diene, and it was shown that such compounds cyclize spontaneously to give isolable cyclopentadiene complexes as precursors to cyclopentadienes.^{12c}



SCHEME 35. Cyclopentadienes via 6-amino-1-metalla-1,3,5-trienes by the "alkyne route."

SCHEME 36. Cyclopenta[*b*]pyrans by two-alkyne insertion.

D. Cyclopenta[*b*]pyrans by Two-Alkyne Insertion

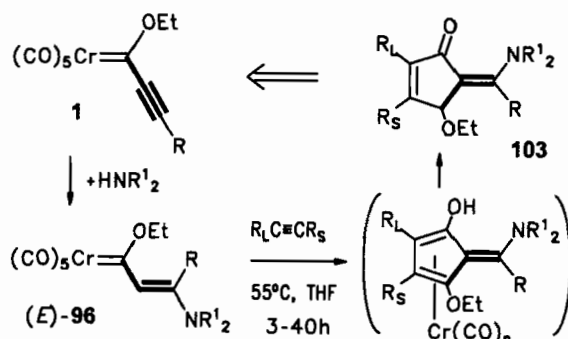
Formation of cyclopenta[*b*]pyrans (= oxapseudoazulenes) **102** is achieved by subsequent insertion of two molecules of alkyne and one carbon monoxide unit into the Cr=C bond of a (2-aminoalkenyl)carbene complex (*E*)-**96** generated from compound **1j'** (Scheme 36).^{9f}

E. 5-Methylenecyclopent-2-enones by [2+2+1] Cycloaddition

Reactions of 4-amino-1-metalla-1,3-dienes, generated from (1-alkynyl)carbene complexes **1** by addition of secondary amines (Scheme 32), with alkynes may lead to production of different compounds, depending on the substitution pattern as well as on the reaction conditions employed.^{3r} Whereas successive addition of a secondary amine and *one* molecule of a *terminal* alkyne to a (1-alkynyl)carbene complex **1j** affords cyclopentadienes (Scheme 35), addition of *two* molecules of a *terminal* alkyne to complex **1j'** yields cyclopenta[*b*]pyrans (Scheme 36). In an extension of this reaction sequence, (methylene)cyclopent-2-enones **103** are obtained from (1-alkynyl)carbene chromium compounds **1** (R = *n*-Pr, Ph, CH₂CH₂CH₂OTBDS) by addition of secondary amines (NR₂¹ = NMe₂, morpholino) and *disubstituted* alkynes (Scheme 37).^{9e}

F. 1,4-Diamino-2-alkoxynaphthalenes via Isocyanide Addition

Addition of cyclohexyl isocyanide to 4-amino-1-chroma-1,3-dienes (*E*)-**96b–e** provides a mild and regiospecific access to 1,4-diamino-2-ethoxy naphthalenes **104** [1-NHc-C₆H₁₁; 4-NRR¹ = NMe₂, (*S*)-2-hydroxymethylpyrrolidinyl, (1*R*,2*S*)-2-methylamino-1-phenyl-1-propanol, *N*-*t*-BuMe] in

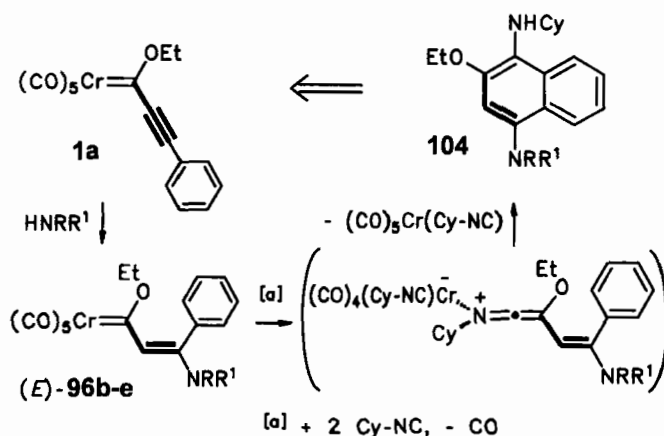


SCHEME 37. 5-Methylene cyclopent-2-enones by [2+2+1] cycloaddition.

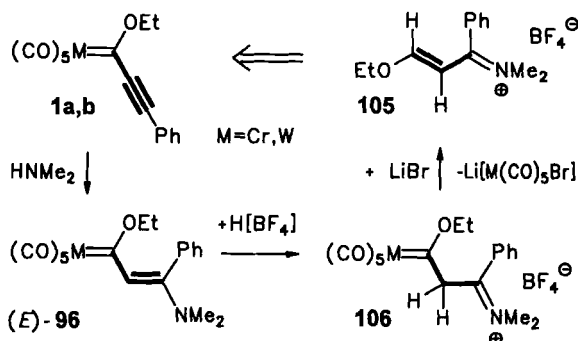
72–85% yield via dienyl ketenimine complexes as key intermediates (Scheme 38).¹¹⁸

G. Iminio(alkyl)carbene Complexes and Alkenyl Iminium Derivatives

Addition of $\text{H}[\text{BF}_4]$ to 4-amino-1-metalla-1,3-dienes (*E*)-**96** in ether leads to precipitation of a stable dialkyliminio(alkyl)carbene complex **106**, which has been characterized by X-ray analysis. Compound **106** is more reactive toward insertion at the $\text{M}=\text{C}$ bond than its precursor (*E*)-**96**. Thus, a marked enhancement of reactivity is achieved by protonation of 4-amino-1-metalla-1,3-dienes. Addition of LiBr to compound **106** and thermolysis



SCHEME 38. 1,4-Diamino naphthalenes by cyclization.

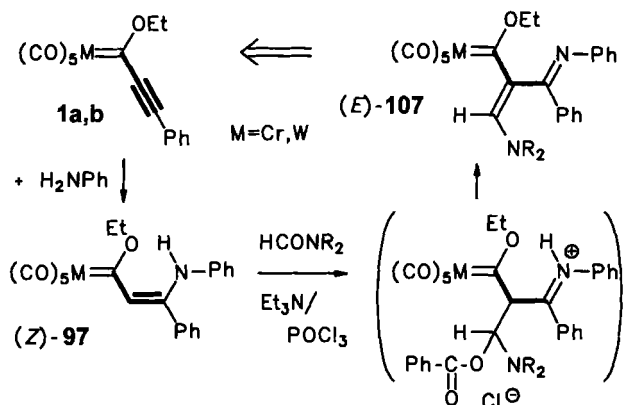


SCHEME 39. Iminio(alkyl)carbene complexes.

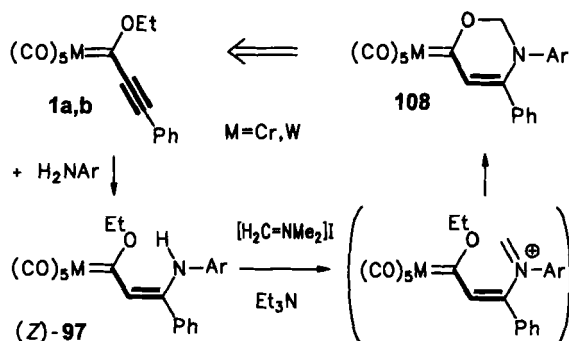
of compound **106**, respectively, afford alkenyl iminium derivatives **105** by disengagement of the metal unit (Scheme 39).¹¹⁹

H. C- and (N,O)-Aminomethylenation of (NH-Enamino)carbene Complexes

A great variety of transformations of (NH-enamino)carbene complexes (**Z**)-**97** become possible because of the presence of hydrogen at the nitrogen atom, which is readily replaced by other functional groups. C-Aminomethylenation of [2-(NH-amino)ethenyl]carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{NHR})\text{Ph}$ (**Z**)-**97** ($\text{M} = \text{Cr}, \text{W}$) with formamides $\text{HCO}-\text{NR}_2$ ($\text{NR}_2 = \text{NMe}_2$, pyrrolidine, morpholine) in the presence of benzoyl chloride and triethylamine affords [2-amino-1-(iminoacyl)ethenyl]carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}[\text{C}(\text{Ph})=\text{NPh}]=\text{CHNR}_2$ (**E**)-**107** in 61–83% yield (Scheme 40). By elimination of carbon monoxide,



SCHEME 40. C-Aminomethylenation.

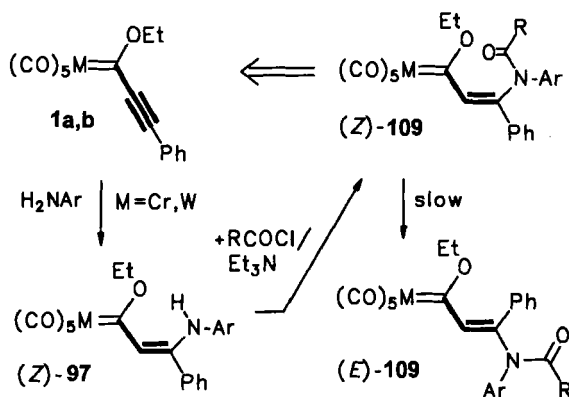
SCHEME 41. *N,O*-Aminomethylenation.

the latter compounds readily form $(\text{CO})_4\text{M}$ chelate complexes, which are stable thermally but are more readily oxidized in air than the corresponding $(\text{CO})_5\text{M}$ complexes to give aminoacrylates in >90% yields.³⁷

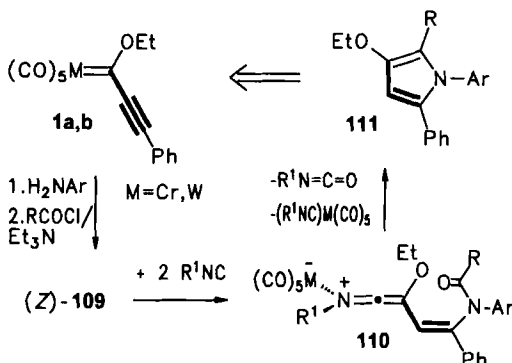
N,O-Aminomethylenation of compounds **(Z)-97** ($\text{M} = \text{Cr}, \text{W}$; $\text{Ar} = \text{Ph}, p\text{-Tol}$) is achieved with *N,N*-dimethylmethyleniminium iodide in the presence of triethylamine and gives oxazin-6-ylidene complexes **108** (60–70%) by *N,O*-ring closure (Scheme 41).³⁷

1. [2-(Acylamino)ethenyl]carbene Complexes by *N*-Acylation of (NH-Enamino)carbene Complexes

N-Acylation of $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{CPh}(\text{NHAr})$ **(Z)-97** ($\text{M} = \text{Cr}, \text{W}$) is observed with $\text{R}-\text{COCl}/\text{Et}_3\text{N}$ ($\text{R} = \text{C}_6\text{H}_5, p\text{-MeOC}_6\text{H}_4, p\text{-NO}_2\text{C}_6\text{H}_4, O\text{-}t\text{-Bu}$) to give compounds $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{CPh}[\text{N}(\text{COR})\text{Ar}]$ **(Z/E)-109** in 72–90% yields with high stereoselectivity (Scheme 42). The



SCHEME 42. [2-(Acylamino)ethenyl]carbene complexes.



SCHEME 43. Pyrroles via fragmentation of ketenimine complexes.

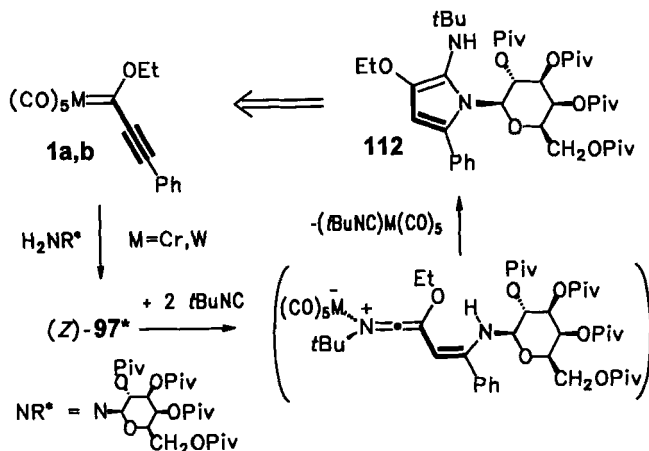
reactivity of the $M=C$ group of compounds **109** is strongly enhanced compared to that of its precursors **97** by the introduction of an *N*-acyl group.¹²⁰

J. 3-Alkoxy Pyrroles via Addition of Isocyanide (or Carbon Monoxide) and Fragmentation of Ketanimines (or Ketenes)

Reaction of compound (Z)-**109** with an isocyanide R^1NC ($R^1 = \text{Cy}, t\text{-Bu}$) at 20°C affords [2-(acylamino)ethenyl]ketanimines $R^1N=C=C(\text{OEt})\text{H}=\text{CPh}[\text{N}(\text{COR})\text{Ar}]$ **110** (>95% yields), which produce pyrroles **111** at $20\text{--}80^\circ\text{C}$ in 90–95% yields by ring-closing metathesis with elimination of an isocyanate (Scheme 43). Pyrroles are also formed on photolysis of compounds (Z)-**109** by insertion of carbon monoxide and subsequent elimination of carbon dioxide. The stereoisomer (*E*)-**109** undergoes an electrocyclic ring closure to 1,4-diaminonaphthalines (>95% yield) in a reaction similar to that shown in Scheme 38, though (because of the electron-withdrawing influence of the *N*-acyl group) under very mild conditions, at 20°C .¹²⁰

K. 2-Amino Pyrroles by Addition of Isocyanide and Cyclization of the Resulting Ketanimines

(*NH*-Enamino)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{CPh}(\text{NHR})$ (Z)-**97** ($M = \text{Cr}, \text{W}$; $R = \text{Ph}, i\text{-Pr}, \text{CH}_2$) add 2 eq of an isocyanide $R^1-\text{NC}$ ($R^1 = c\text{-C}_6\text{H}_{11}, t\text{-Bu}$) to give ketenimine complexes and finally ketanimines, which are readily cyclized to (air-sensitive) 2-amino-3-ethoxypyrroles.¹²¹ Galactopyranosyl pyrroles **112** are obtained by this procedure from enantiomeric pure (2-aminoethenyl)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{CPh}(\text{NHR})$.



SCHEME 44. 2-Aminopyrroles by cyclization of ketenimine complexes.

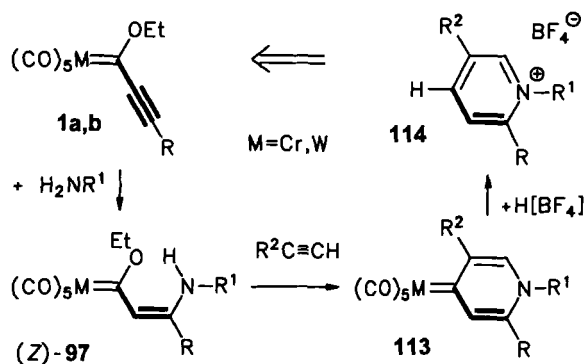
$\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{Ph})\text{NHR}^*$ (*Z*)-**97*** ($\text{R}^* = 2,3,4,6\text{-tetra-}O\text{-pivaloyl-}\beta\text{-D-galactopyranosyl}$, $\text{M} = \text{Cr}, \text{W}$), generated by addition of galactopyranosylamine R^*-NH_2 to the corresponding (1-alkynyl)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}\equiv\text{CPh}$ **1a,b** (Scheme 44).¹¹⁶

L. Pyridinium Compounds and Pyridines by Cycloaddition of an Alkyne

Reaction of (*NH*-enamino)carbene complexes (= 4-amino-1-metalla-1,3-diene) $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{R})\text{NHR}^1$ (*Z*)-**97** ($\text{M} = \text{Cr}, \text{W}$; $\text{R}, \text{R}^1 = \text{Ph}, \text{Me}, i\text{-Pr}, n\text{-Bu}, \text{CH}_2\text{Ph}, \text{CH}_2\text{OMe}$) with an alkyne $\text{R}^2\text{C}\equiv\text{CH}$ ($\text{R}^2 = n\text{-Bu}, \text{Ph}, \text{CH}_2\text{OMe}$) affords (stable) 1,4-dihydro-4-pyridinylidene complexes **113**, which on protonation with HBF_4 yield pyridinium compounds **114** (Scheme 45). Pyridines also are obtained by this route from (*NH*₂-enamino)carbene complexes.^{91,9g}

M. 1-Aza-1,3-butadiene Complexes via 1,4- and *N*-Alkenyl(amino)carbene Chromium Complexes via 1,5 Hydrogen Shifts

Thermolysis of (*NH*-enamino)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{R})\text{NHR}^1$ ($\text{M} = \text{Cr}, \text{W}$) was shown to afford 1-aza-1,3-butadienes $(\text{EtO})\text{HC}=\text{CH}-\text{CR}=\text{NR}^1$ by a 1,4 hydrogen shift. The latter are readily hydrolyzed on alumina to give the corresponding aldehydes $\text{OHC}-\text{CH}-\text{CR}=\text{NR}^1$.^{91,122} Thermolysis of an (*NH*₂-enamino)carbene chromium complex $(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{R})\text{NH}_2$ (*Z*)-**97** ($\text{R} = n\text{-Pr}, c\text{-Pr}, t\text{-Bu}$,

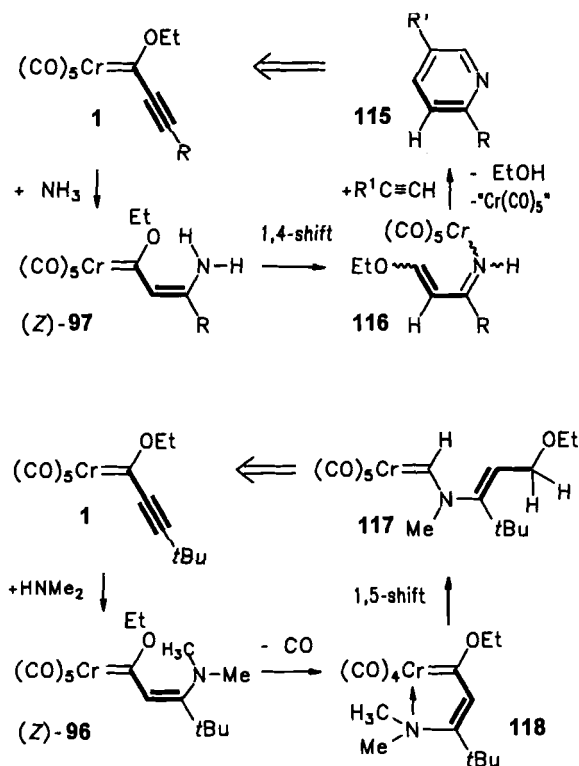
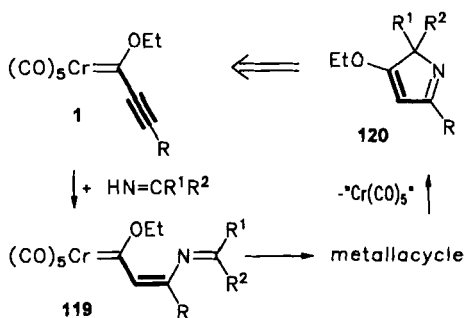


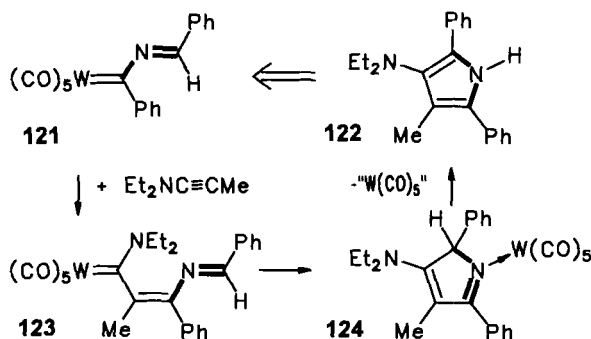
SCHEME 45. Pyridinium compounds by addition of alkynes.

Ph) yields 1-aza-butadiene complexes **116**, which were isolated and shown to produce pyridines **115** on reaction with an alkyne $\text{R}^1\text{C}\equiv\text{CH}$ ($\text{R}^1 = n\text{-Pr, Ph}$) (Scheme 46).^{9g} Interestingly, the (NMe_2 -enamino)carbene complex $(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})-\text{CH}=\text{C}(t\text{-Bu})\text{NMe}_2$ (**Z**)-**96** undergoes a 1,5 hydrogen shift from the $\text{N}-\text{CH}_3$ group, as well as a migration of the metal unit (via a chelate complex **118**) to give an (amino)carbene complex **117**.⁹ⁱ

N. 2H-Pyrroles via 5-Aza-1-chroma-1,3,5-trienes ("Imine Route")

Reaction of imines with an alkoxy-carbene complex affords (1-imino)carbene complexes, albeit in low yields.^{123,124} Because the latter compounds are interesting building blocks for organic synthesis^{125,12d} more efficient methods for their preparation have been developed.¹²⁶⁻¹³² Addition of imines to (1-alkynyl)carbene complexes **1** was found to occur at the $\text{C}\equiv\text{C}$ as well as at the $\text{M}=\text{C}$ bond. Ketimines $\text{R}^1\text{R}^2\text{C}=\text{NH}$ ($\text{R}^1, \text{R}^2 = \text{Ph, } p\text{-MeOC}_6\text{H}_4, c\text{-Pr}$) form 1,4-adducts (= 1-chroma-5-aza-1,3,5-trienes) **119** with (1-alkynyl)carbene complexes **1** ($\text{R} = n\text{-Pr, } c\text{-Pr, } t\text{-Bu}$) at 25°C in 41–98% yield. These adducts cyclize at $50\text{--}55^\circ\text{C}$ to give 2H-pyrroles **120** ("imine route" to pyrroles).¹³³ A 1-chroma-4-azacyclohexa-2,4-diene was suggested as an intermediate (Scheme 47). Kinetic studies on the addition of imines^{133,23} were interpreted in terms of a two-step process with a polar transition state for the rate-determining step. A correlation between reactivity and pK_a was found for anilines,¹³⁴ and the influence of solvent polarity was studied for pyrazole.¹³⁵

SCHEME 46. 1-Azabutadiene and *N*-alkenyl(amino)carbene chromium complexes.SCHEME 47. 2*H*-Pyrroles via the "imine route."



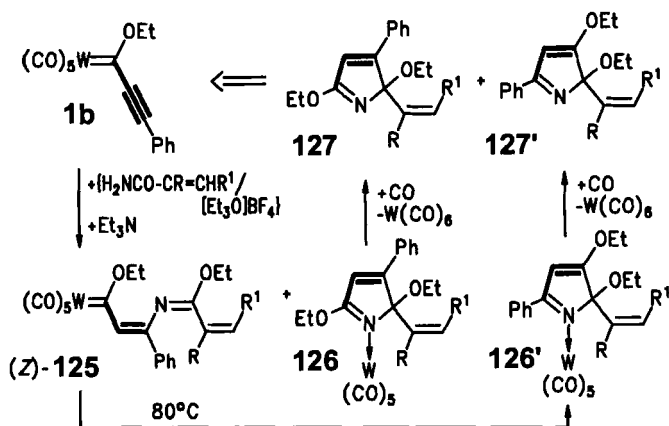
SCHEME 48. Pyrroles via the "alkyne route."

O. 2H-Pyrroles via 5-Aza-1-metalla-1,3,5-trienes ("Alkyne Route")

A further approach to the synthesis of pyrroles other than that shown in Scheme 47 involves formation of 1-metalla-5-aza-1,3,5-trienes **123** ($\text{M} = \text{W}$) by insertion of an alkyne into the $\text{M}=\text{C}$ bond of an (imino)carbene complex **121**, leading to chain extension by two carbon atoms ("alkyne route" to pyrroles). Compounds **123** cyclize spontaneously to 2H-pyrrole complexes **124**, from which 1H-pyrroles **122** are obtained by disengagement of the metal unit (Scheme 48).^{12d} 2H-Pyrrole complexes of type **124** have been characterized by X-ray analysis, and 2H-pyrroles could be eliminated from such complexes if substituents other than hydrogen are attached to C2 of the compound.^{136,125,137,12a,12b}

P. 5-Aza-1-metalla-1,3,5,7-octatetraenes and 2H-Pyrroles via Addition of Primary Alkenylimidates

A very efficient approach to the synthesis of 5-aza-metallapolyenes is based on reactions of acid amides with (1-alkynyl)carbene complexes. Thus, addition of *primary* alkenyl imidates, generated *in situ* by alkylation of primary alkenyl amides $\text{R}^1\text{CH}=\text{CR}-\text{CONH}_2$ with $[\text{Et}_3\text{O}]\text{BF}_4$, to (1-alkynyl)carbene tungsten complex **1b** affords 5-aza-1-metalla-1,3,5,7-octatetraenes $(\text{CO})_5\text{W}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{Ph})-\text{N}=\text{C}(\text{OEt})-\text{CR}=\text{CHR}^1$ (*Z*)-**125** ($\text{R}, \text{R}^1 = \text{H}, \text{Me}, \text{Ph}$) in 60–80% yield, together with 2H-pyrrole complexes **126** in 12–20% yield and dihydroazete complexes. Compounds **125** and **126** are generated by competing reactions of imidate at the $\text{M}=\text{C}$ and $\text{C}\equiv\text{C}$ bond of complex **1b**. Interestingly, cyclization of compounds (*Z*)-**125** at 80°C results in formation of 2H-pyrrole complexes **126'**, from which 2H-pyrroles **127'** are generated. The latter, which are regioisomers



SCHEME 49. 5-Aza-1-metalla-1,3,5,7-octatetraene and 2H-pyrroles via addition of primary alkenylimides.

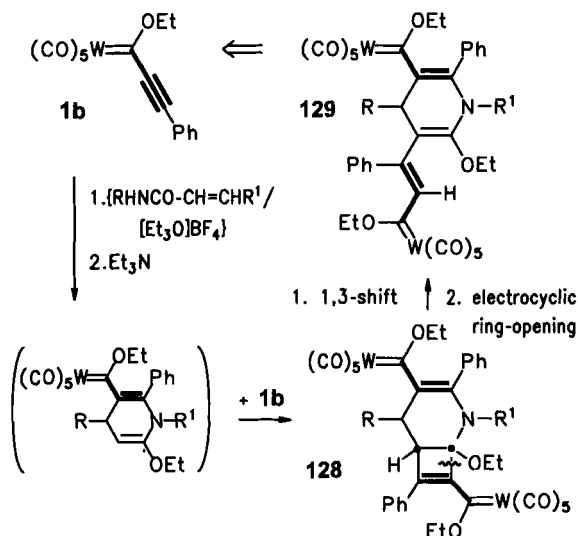
of the 2H-pyrroles **127**, are generated by disengagement of the metal unit (Scheme 49).¹³⁸

Q. Binuclear Dihydropyridinyl Carbene Complexes by [4+2] Addition of Secondary Alkenyl Amides

Addition of *secondary* alkenyl imidates, generated *in situ* by alkylation of secondary alkenyl amides $\text{R}^1\text{CH}=\text{CH}-\text{CONHR}$ ($\text{R} = \text{Me}, i\text{-Pr}$; $\text{R}^1 = \text{Me}, \text{Ph}$) with $[\text{Et}_3\text{O}]\text{BF}_4$ and subsequent treatment with Et_3N , to (1-alkynyl)carbene-tungsten complex **1b** affords (dihydropyridinyl)carbene complexes **128** resulting from regioselective [4+2] cycloaddition of the imide and [2+2] cycloaddition of a second molecule of **1b**. Compounds **128**, in the presence of silica gel, undergo facile ring opening of the four-membered ring, which leads to binuclear 5-aza-1,11-dimetalla-1,3,6,8,10-pentaenes **129**, in which two metal centers are connected by π conjugation (Scheme 50). Compounds **128** and **129** have been characterized by X-ray analysis.¹³⁹

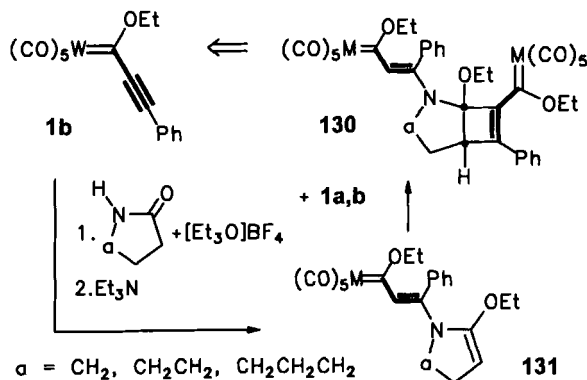
R. Divinyl Enamino Carbene Complexes (= 4-Enamino-1-metalla-1,3-dienes) by N-Addition of Enamines

Addition of secondary *alkyl* imidates, generated *in situ* by ethylation of secondary cycloalkyl amides $^{\text{L}}\text{a}-\text{CH}_2\text{CH}_2-\text{CONH}^{\text{L}}$ ($\text{a} = \text{CH}_2, \text{CH}_2\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}_2$) with $[\text{Et}_3\text{O}]\text{BF}_4$ and subsequent treatment with Et_3N , to

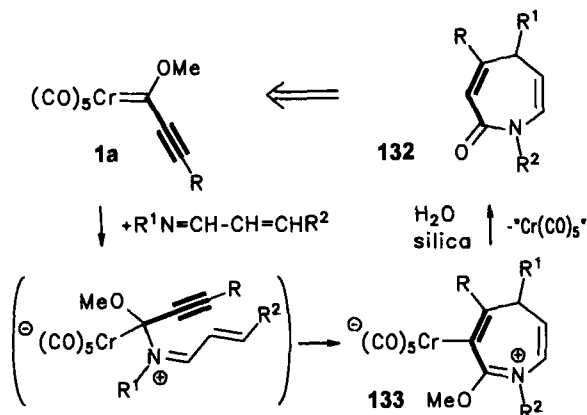


SCHEME 50. Dihydropyridinyl carbene complexes via [4+2] cycloaddition of secondary alkenylimidates.

(1-alkynyl)carbene tungsten complex **1b** affords 4-enamino-1-metalla-1,3-dienes (= 4-aza-1-metalla-1,3,6-heptenes) **131** resulting from regioselective *N*-addition of the imidate to the $\text{C}\equiv\text{C}$ bond of compound **1b**, with concomitant elimination of a proton from the α -carbon atom. In a subsequent [2+2] cycloaddition a second molecule of **1b** is added to compound **131** to give a bicyclic heterocyclic ring system **130** in high yield (Scheme 51).¹⁴⁰



SCHEME 51. 4-Enamino-1-metalla-1,3-dienes.



SCHEME 52. Azepinones by [4+3] cycloaddition of azadienes.

S. Azepinones via [4+3] Cycloaddition of Azadienes

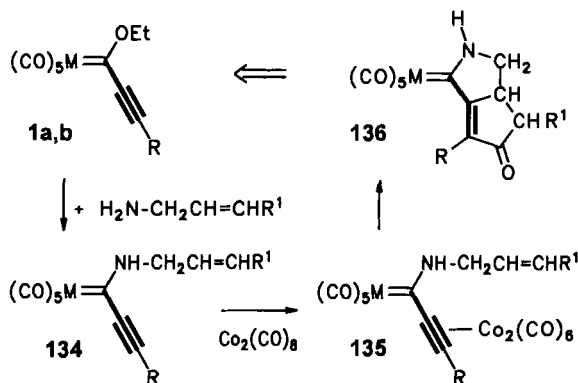
The reaction of an azadiene $\text{R}^1\text{N}=\text{CH}-\text{CH}=\text{CHR}^2$ ($\text{R} = \text{Ph, Me}$; $\text{R}^2 = n\text{-Pr, Bn, } i\text{-Pr, } n\text{-Pr}$) with a (1-alkynyl)carbene *chromium* complex **1a** ($\text{R} = \text{Ph, SiMe}_3, t\text{-Bu}$) quite unexpectedly affords [4+3] cycloaddition products **133** in 57–93% yield, from which azepinones **132** are obtained on contact with wet silica (Scheme 52).¹⁴¹ Reaction of azadienes $\text{R}^1\text{N}=\text{CH}-\text{CH}=\text{CHR}^2$ ($\text{R} = \text{Ph, Me}$; $\text{R}^2 = n\text{-Pr, Bn, } i\text{-Pr, } n\text{-Pr}$) with a (1-alkynyl)carbene *tungsten* complex **1b** ($\text{R} = \text{Ph}$) was shown to produce 1,4-dihydropyridine complexes (of the type shown in Scheme 50) as the major products.¹⁴²

T. Cyclopentenone Derivatives via Pauson–Khand Cyclization

Pauson–Khand cyclization^{3k,143} of *N*-allyl (1-alkynyl)carbene complexes **134** ($\text{M} = \text{Cr, W}$; $\text{R} = \text{Ph, Et}$; $\text{R}^1 = \text{H, Me}$) affords cyclopentenone derivatives **136**¹⁴⁴ via cobalt complexes **135**¹⁴⁵ (Scheme 53), as well as chromium complexes.¹⁴⁶ Cyclopentenones also have been derived from *N*-diallyl(1-alkynyl)carbene complexes.³⁹ Stable cobalt complexes of type **135** are obtained from *O*-allyl (1-alkynyl)carbene complexes. Interestingly, the last-named compounds do not form a cyclopentenone on heating; instead, they form an “enyne” by elimination of $\text{M}(\text{CO})_6$ in a “retro-Fischer reaction.”¹⁴⁷

U. Indolines via Moore-Type Cyclization

Thermolysis of a bis(alkynyl)carbene complex **137** in the presence of a hydrogen source affords an indoline **138** via 1,4-diradical intermediates in

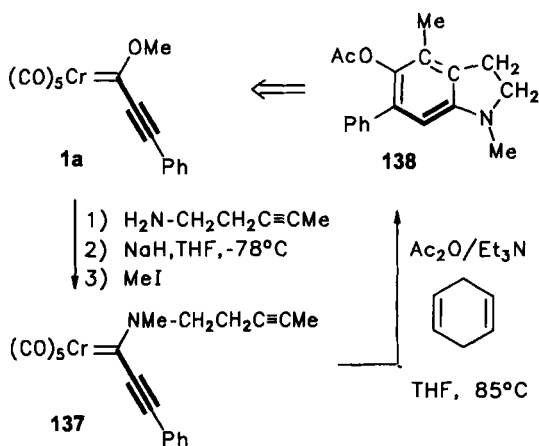


SCHEME 53. Cyclopentenone derivatives via Pauson-Khand cyclization.

a metal-mediated Moore-type cyclization of an enynyl ketene complex (Scheme 54).¹⁴⁸

V. Hydrazinocarbene, Imidate, and Pyrazolidinyldene Complexes via Hydrazinolysis

Hydrazinolysis of (alkoxy)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{R}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) has been studied much less than the aminolysis of such compounds.^{149–152} Usually, hydrazinolysis takes a nonuniform course and yields several seemingly different products. The preparation of (hydrazino)-



SCHEME 54. Indolines.

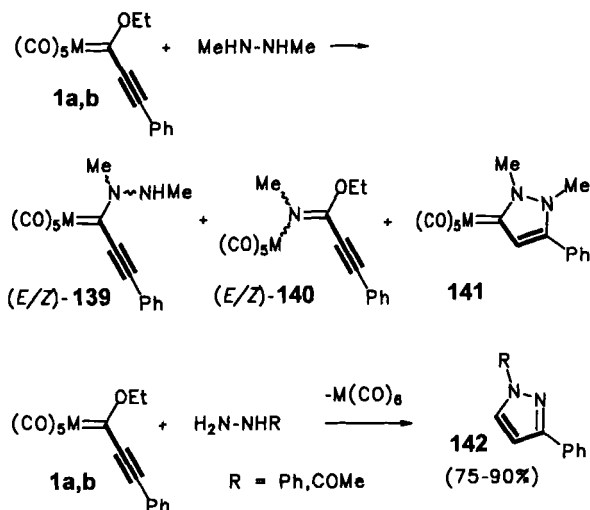
carbene complexes by 1-addition of hydrazines to allenylidene complexes has been described.^{126,153} As a consequence of the ambidentate character of both the hydrazines and the (1-alkynyl)carbene complexes, a diversity of parallel reactions can be anticipated if these compounds are reacted together. Hydrazinolysis of (1-alkynyl)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}\equiv\text{CPh}$ **1a,b** ($\text{M} = \text{Cr}, \text{W}$) with mono- and 1,2-dimethylhydrazine $\text{MeHN}-\text{NHR}$ ($\text{R} = \text{Me}, \text{H}$) affords three different compounds: hydrazinocarbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{NMe}-\text{NHR})-\text{C}\equiv\text{CPh}$ (*E/Z*)-**139**, imidate complexes $(\text{CO})_5\text{M}[\text{MeN}=\text{C}(\text{OEt})-\text{C}\equiv\text{CPh}]$ (*E/Z*)-**140**, and pyrazolidinyldene complexes **141**. Hydrazinolysis of **1** with 1,1-dimethylhydrazine or (unsubstituted) hydrazine $\text{H}_2\text{N}-\text{NR}_2$ ($\text{R} = \text{Me}, \text{H}$) yields, in addition to hydrazinocarbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{NH}-\text{NR}_2)-\text{C}\equiv\text{CPh}$, imidate complexes $(\text{CO})_5\text{M}[\text{HN}=\text{C}(\text{OEt})-\text{C}\equiv\text{CPh}]$ and a benzonitrile complex $(\text{CO})_5\text{M}(\text{N}\equiv\text{CPh})$. Hydrazinolysis of **1** with $\text{H}_2\text{N}-\text{NHR}$ ($\text{R} = \text{COMe}, \text{Ph}$) gives pyrazoles **142** as the only products (Scheme 55). Reaction of **1** with *N*- and *O*-methylhydroxylamines affords imidate complexes only.⁴⁶ For related reactions, see Refs. 153, 154. Oxidative cleavage of $\text{M}=\text{C}$ bonds of (1-alkynyl)carbene complexes and other Fischer carbene complexes was also achieved with dimethyl dioxirane,¹⁵⁵ sulfilmines,^{156,157} phosphorus ylides,¹⁵⁸⁻¹⁶¹ nitrogen ylides,¹⁶² and sulfur ylides.¹⁶³

W. Dihydrofuran-2-ylidene Complexes

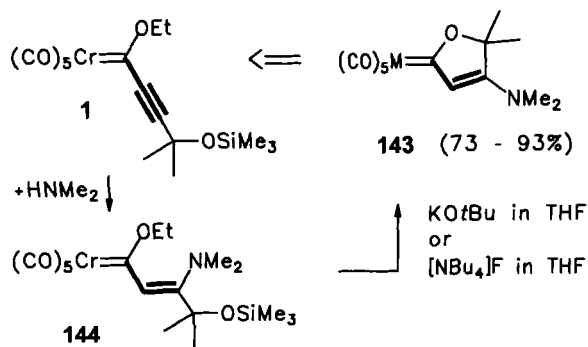
Formation of dihydrofuran-ylidene complexes **143** was achieved in 73–93% yield by addition of HNMe_2 and subsequent cyclization after hydrolysis of the $\text{O}-\text{Si}$ bond of **144** (Scheme 56).^{9b}

X. Phosphonium Allenide Complexes by Addition of Tertiary Phosphanes

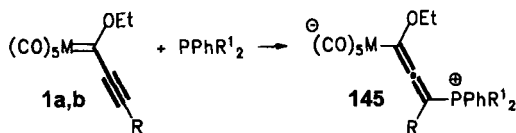
Reactions of carbene complexes with phosphorous compounds are topics of current research.¹⁶⁴⁻¹⁶⁷ (1-Alkynyl)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}\equiv\text{CR}$ **1** ($\text{M} = \text{Cr}, \text{W}$; $\text{R} = \text{Ph}, t\text{-Bu}, \text{SiMe}_3$) readily add tertiary phosphanes PPhR'_2 ($\text{R}' = \text{Ph}, \text{Me}$) and form stable zwitterionic phosphonium allenide complexes $^-(\text{CO})_5\text{M}-\text{C}(\text{OEt})=\text{C}=\text{C}(\text{R})-\text{P}^+\text{PhR}'_2$ **145**, which have been characterized by X-ray diffraction (Scheme 57).⁵⁵ In previous studies on Michael-type additions of nitrogen and oxygen nucleophiles to (1-alkynyl)carbene complexes **1**, zwitterionic allenide complexes of type **145** have been postulated as intermediates.^{21,23,50a,62,112,168,169} Unambiguous structural evidence of the tendency to form such intermediates is given by isolation of a stable zwitterionic adduct, such as compound **145**. Zwitterionic



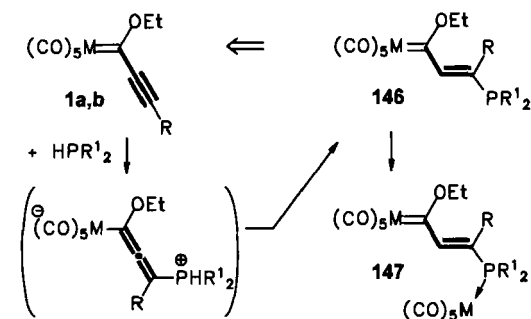
SCHEME 55. Hydrazinolysis: 1-substitution, insertion, and cyclization.



SCHEME 56. Dihydrofuran-2-ylidene complexes.



SCHEME 57. Phosphonium allenide complexes.

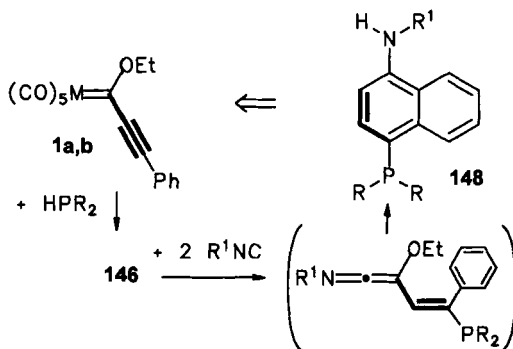


SCHEME 58. [(2-Phosphanyl)ethenyl]carbene complexes.

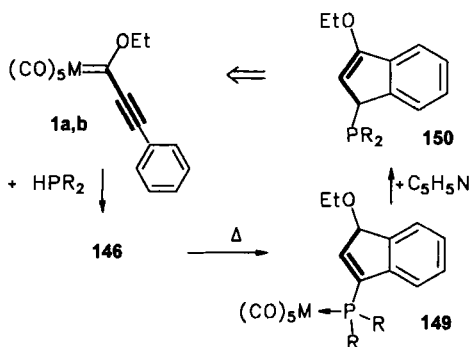
allenylidene complexes of different type are obtained by 1-addition of phosphanes to allenylidene chromium complexes.^{170,171}

Y. [(2-Phosphanyl)ethenyl]carbene Complexes by Addition of Secondary Phosphanes

Addition of *secondary* phosphanes HPR^1_2 to compounds **1a,b**, ($\text{M} = \text{Cr}$, W ; $\text{R} = \text{Ph}$) affords [2-(phosphanyl)ethenyl]carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{R})\text{PR}^1_2$ (*E*)-**146** ($\text{R}^1 = t\text{-Bu}$, $c\text{-C}_6\text{H}_{11}$, Ph) in 34–89% isolated yields. Binuclear complexes $[(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{R})\text{PR}_2] \text{M}(\text{CO})_5$ (*E*)-**147** are obtained as by-products. X-ray data of the prototypic compounds are reported (Scheme 58).⁵⁵



SCHEME 59. 2-Phosphino naphthalenes.



SCHEME 60. Phosphinoindenones.

Z. 1-Amino-2-ethoxy-4-phosphino Naphthalenes and Phosphinoindenones

1-Amino-2-ethoxy-4-phosphino naphthalenes **148** (>90% yields) are obtained from phenylalkynyl carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}\equiv\text{CPh}$ ($\text{M} = \text{Cr}, \text{W}$) **1** by a novel two-step carbene/alkyne benzannulation. The first step involves the formation of [(*E*)-(2-phosphino)ethenyl]carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{Ph})\text{PR}_2$ (*E*)-**146** by 4-addition of secondary phosphines HPR_2 ($\text{R} = t\text{-Bu}, c\text{-C}_6\text{H}_{11}$) to **1**. A subsequent addition of an isocyanide $\text{R}^1\text{-NC}$ ($\text{R}^1 = t\text{-Bu}, c\text{-C}_6\text{H}_{11}$) to (*E*)-**146** yields a ketene imine complex $(\text{CO})_5\text{M}[\text{R}^1\text{N}=\text{C}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{R})\text{PR}_2]$ and finally, by ligand displacement, a ketene imine that cyclizes spontaneously to **148** (Scheme 59).¹⁷²

Thermolysis of (*E*)-**146** affords a phosphinoindene $(\text{CO})_5\text{M}$ complex **149**, from which a metal-free phosphinoindene **150** is obtained (Scheme 60).¹⁷²

V

REACTION WITH OXYGEN AND SULFUR NUCLEOPHILES

Addition of protic oxygen nucleophiles $\text{R}-\text{OH}$ ($\text{R} = \text{alkyl}, \text{alkenyl}, \text{aryl}, \text{acyl}$) to (1-alkynyl)carbene complexes **1** may in principle follow the reaction paths outlined in Scheme 61.

A. 2,4-Dioxy-1-metalla-1,3-butadienes and 3-Oxy-1-metalla-1,2,3-butatrienes by Alcoholysis

Substitution of the alkoxy substituent of a (1-alkynyl)carbene complex **1** has been briefly mentioned for only one case, in which the methoxy

TABLE VI
 ^{13}C NMR SHIFTS (δ VALUES) AND IR FREQUENCIES (cm^{-1} , HEXANE) OF SELECTED
 ALKOXY(2-OXYETHENYL)CARBENE COMPLEXES $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{CH}=\text{C}(\text{OR})\text{R}^1$

M	R ¹	R	Cfg ^a	S ^b	$\delta(\text{C1})$	$\delta(\text{C2})$	$\delta(\text{C3})$	$\nu(\text{C}\equiv\text{O})^c$	Ref.
Cr	Ph	Me	<i>E</i>	^d	323.6	118.6	158.1	—	173b
Cr	Ph	Et	<i>E</i>	^f	323.6	120.6	159.5	—	168
			<i>Z</i>	^f	323.0	124.4	152.0	2056, 1977, 1940	168
Cr	Ph	Glu ^g	<i>E</i>	^f	327.1	122.5	156.7	2057, 1978, 1942	168
			<i>Z</i>	^f	327.0	122.9	149.8	2057, 1977, 1942	168
Cr	<i>c</i> -Pr	Me	<i>E</i>	^f	318.2	120.4	165.6	—	20
Cr	Ph	Ph	<i>E</i>	^f	328.5	130.1	154.1	2056, 1980, 1944	103
Cr	Ph	PhCO	<i>Z</i>	^f	334.2	134.1	139.4	2059, 1986, 1946	169
W	Ph	<i>i</i> -Pr	<i>E</i>	^e	322.4	122.2	160.9	—	173b
W	Ph	Et	<i>E</i>	^e	300.8	125.5	159.0	—	168
			<i>Z</i>	^e	300.9	126.7	154.0	2065, 1976, 1939	168
W	Ph	PhCO	<i>Z</i>	^f	305.7	134.1	142.6	2067, 1982, 1945	169
W	<i>t</i> -Bu	<i>t</i> -BuCO	<i>E</i>	^f	311.4	131.0	150.6	2068, 1984, 1943	36
			<i>Z</i>	^f	331.5	131.1	144.9	2057, 1980, 1946	103
W	Ph	Ph	<i>E</i>	^f	300.7	130.4	154.0	2065, 1983, 1942	103
W	Ph	Ph	<i>Z</i>	^f	303.8	131.2	148.5	2065, 1983, 1944	103

^a Configuration.

^b Solvent of ^{13}C NMR spectrum.

^c In hexane.

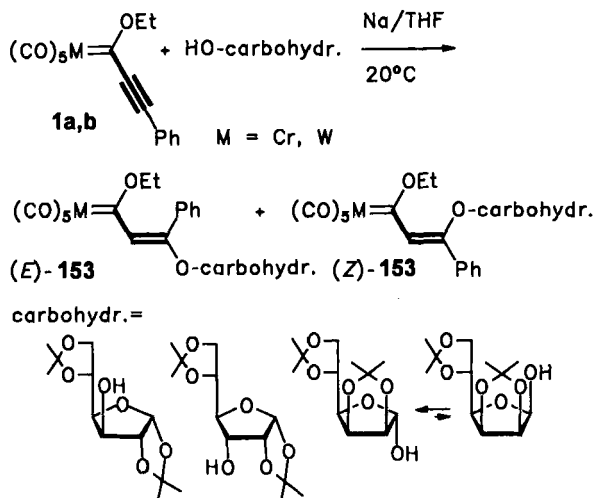
^d In CDCl_3 .

^e In CD_3COCD_3 .

^f In C_6D_6 .

^g Glu = 1,2:5,6-di-*O*-isopropyliden- α -D-glucofuranose.

$\text{C}(\text{OMe})-\text{CH}_3$ with an ortho ester;¹⁷⁵ (iii) the condensation of aryl- or alkylcarbene complexes with enolizable acid amides $\text{RCH}_2-\text{CONR}_2$, a reaction involving insertion of the $\text{C}-\text{CN}$ unit of the acid amide into the $\text{M}=\text{C}$ bond;¹⁷⁶ (iv) the insertion of an alkyne into the $\text{M}=\text{C}$ bond of an (alkoxy)carbene complex;^{3b,177,174} and (v) the base-catalyzed addition of an alcohol to a (1-alkynyl)carbene complex.^{9g,168,173} The last reaction has



SCHEME 62. Carbene complexes of carbohydrates.

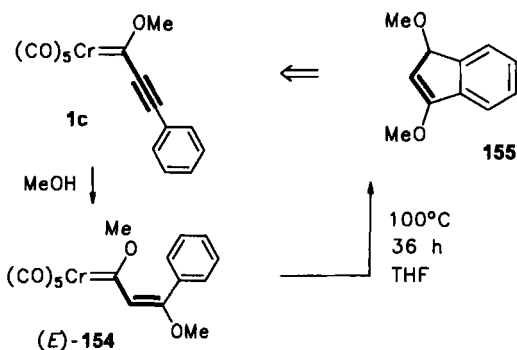
been applied, for example, for the introduction of carbohydrates as chiral inductors into alkenylcarbene complexes. 1,2:5,6-Di-*O*-isopropyliden- β -glucofuranose, 1,2:5,6-di-*O*-isopropyliden- α -D-allofuranose, and 2,3:5,6-di-*O*-isopropyliden- α -D-mannofuranose add regiospecifically at C3 of a (1-alkynyl)carbene complex **1a,b** to give enol ether complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{Ph})-\text{O}(\text{carbohydrate})$ **153** and a minor amount of the propa-1,2-dien-1-yl carbene complex $(\text{CO})_5\text{W}=\text{C}=\text{C}=\text{C}(\text{OEt})\text{Ph}$ (Scheme 62).^{168,223}

The [(2-alkoxy)ethenyl]carbene complexes are obtained as *E/Z* mixtures, in which the (*E*)-stereoisomers predominate. Other carbene complexes, in which carbohydrates are bonded directly to the metal center¹⁷⁸ or to the carbene carbon atom,^{179,180} are also known.

Thermolysis of the pentacarbonyl chromium compounds **151** affords tetracarbonyl chelate complexes by loss of a *cis* CO group,²⁰ in the same fashion that has been found for *ortho*-alkoxy phenylcarbene complexes¹⁸¹ and similar products.¹⁸² The $\text{C}\equiv\text{C}$ triple bond of alkoxy(1-alkynyl)carbene complexes **1** is more reactive than that of amino(1-alkynyl)carbene complexes. $(\text{CO})_5\text{Cr}=\text{C}(\text{NHMe})-\text{C}\equiv\text{CPh}$ was shown to add ethanol very slowly to give $(\text{CO})_5\text{Cr}=\text{C}(\text{NHMe})-\text{CH}=\text{C}(\text{OEt})\text{Ph}$ in 79% yield.²¹

C. Dialkoxyindenes by Cyclization of 2,4-Dialkoxy-4-phenyl-1-chroma-1,3-dienes

Thermally induced cyclization of the 1-methoxy-3-phenyl-[(2-methoxy)-alkenyl]carbene-chromium complex [= 2,4-dimethoxy-4-phenyl-1-(penta-



SCHEME 63. Cyclization to dialkoxindenes.

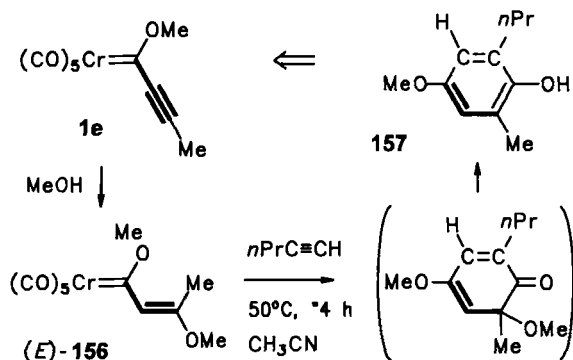
carbonyl)chroma-1,3-diene] (*E*)-**154** affords a dimethoxyindene **155** in 73% yield (Scheme 63).¹⁸³

D. Hydroquinones by Reaction of 2,4-Dialkoxy-4-alkyl-1-chroma-1,3-dienes with an Alkyne

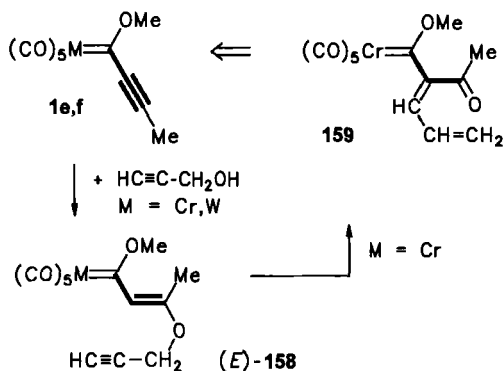
Reaction of 2,4-dimethoxy-4-phenyl-1-(pentacarbonyl)chroma-1,3-diene (*E*)-**156** with 1-pentene leads to production of a hydroquinone **157** in 64% yield (Scheme 64).¹⁸⁴

E. 1-Metalla-1,3,5-trienes via [3,3'] Rearrangement

Addition of propargylic alcohol to a (1-alkynyl)carbene complex **1e,f** ($M = \text{Cr}, \text{W}$) affords the enol ether adduct (*E*)-**158**, whose chromium



SCHEME 64. Hydroquinones by alkyne insertion.



SCHEME 65. Metallatrienes by oxy-cope rearrangement.

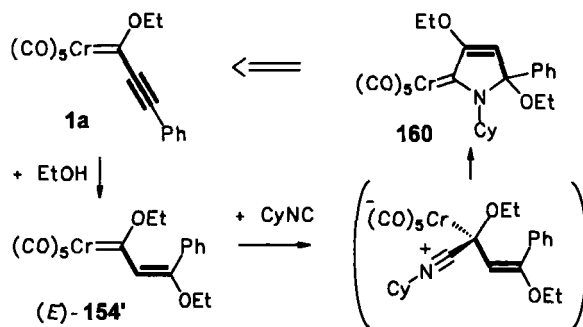
complex undergoes hydrogen migration and [3,3'] rearrangement to give a 1-chroma-1,3,5-triene **159** in 62% yield (Scheme 65).¹⁸⁵

F. Dihydropyrrolylidene Complexes by Insertion of Isocyanide

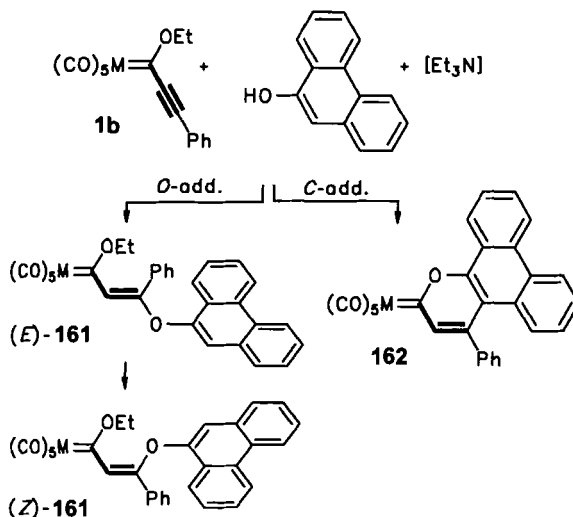
[2-(Alkoxy)ethenyl]carbene complexes easily undergo insertion of an isocyanide into the $\text{M}=\text{C}$ bond.^{3q,119} Reaction of cyclohexyl isocyanide with [2-(alkoxy)ethenyl]carbene complex (E)-**154** yields a 4,5-dihydropyrrolylidene complex **160** (Scheme 66),¹⁶⁹ in agreement with earlier observations of similar reactions of related carbene complexes.^{174b,186}

G. Addition of Phenols

Phenol and 2-naphthol provide [2-(aryloxy)ethenyl]carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{OAr})\text{Ph}$ ($\text{M} = \text{Cr, W}$; $\text{Ar} = \text{Ph, 2-naphthyl}$)



SCHEME 66. 4,5-Dihydropyrrolylidene complexes.

SCHEME 67. *O*- and *C*-alkenylation of 9-phenanthrol.

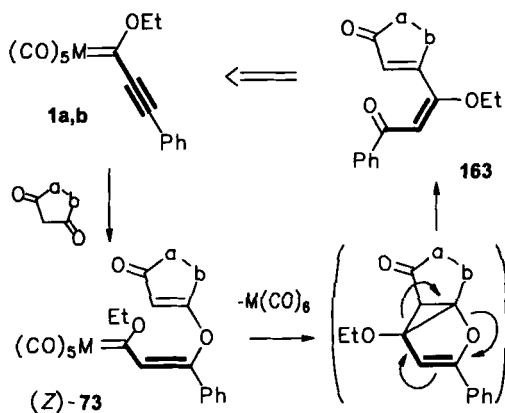
in 81–91% yield. The addition is highly regio- and stereoselective and affords (*E*)-stereoisomers initially, which undergo (*E/Z*) isomerization in solution to give (*Z*)-isomers.¹⁰³ Both *O*- and *C*-addition products, **161** and **162**, respectively, are derived from reaction of 9-phenanthrol with (1-alkynyl)carbene complex **1** in the ratio 2 : 1 (Scheme 67).¹⁰³ *O*- and *C*-addition products have been also obtained from addition of enolizable carbonyl compounds to (1-alkynyl)carbene complexes (Scheme 23).¹⁰³

H. Dienediones by Divinyl Ether Fragmentation

[2-(Alkenyloxy)ethenyl]carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{O-alkenyl})\text{Ph}$ **76** ($\text{M} = \text{Cr}, \text{W}$), obtained by base-catalyzed *O*-addition of enolizable 1,3-diones (cyclopentan-1,3-dione and dimedone, $\text{a}, \text{b} = \text{CH}_2\text{CH}_2$ and $\text{CH}_2\text{CMe}_2\text{CH}_2$) to (1-alkynyl)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}\equiv\text{CPh}$ **1a,b** ($\text{M} = \text{Cr}, \text{W}$) (Scheme 23), undergo thermal fragmentation to give dienediones **163**, resulting from an overall C_3 insertion of the (1-alkynyl)carbene ligand of **1** into a C,O bond of the enolizable 1,3-dione (Scheme 68).¹⁰³

I. (Amino)ketocarbene Complexes and Acid Amides

Addition of cyclohexyl isocyanide to enol ether **164** derived from addition of phenol to a (1-alkynyl)carbene complex **1a** results in formation of a

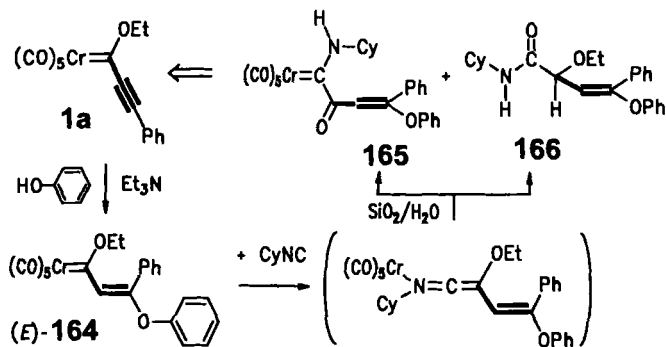


SCHEME 68. Dienediones by divinyl ether fragmentation.

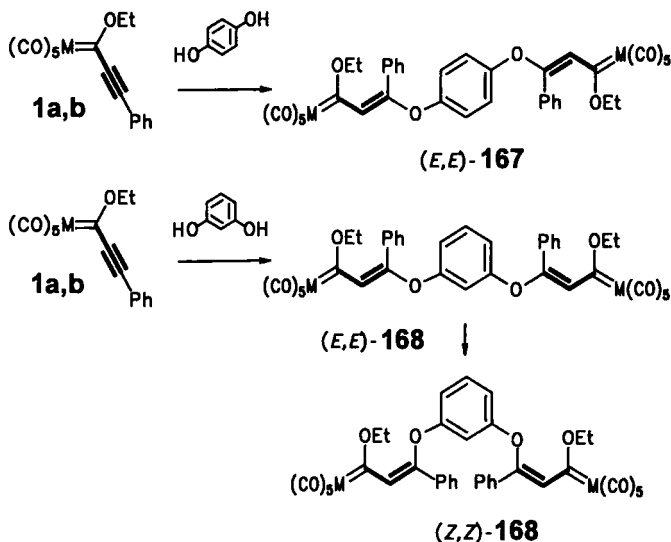
ketene imine complex $(\text{CO})_5\text{Cr}[\text{CyN}=\text{C}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{OPh})\text{Ph}]$, which in the presence of water on silica affords an (1-amino)ketocarbene complex $(\text{CO})_5\text{Cr}=\text{C}(\text{NHCy})-\text{C}(=\text{O})-\text{CH}=\text{C}(\text{OPh})\text{Ph}$ **165** and an amide $(\text{CyNH})-\text{C}(=\text{O})-\text{CH}(\text{OEt})-\text{CH}=(\text{OPh})\text{Ph}$ **166** (Scheme 69).¹⁰³

J. Binuclear Carbene Complexes

Binuclear carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{Ph})-\text{O}-\text{Ar}-\text{O}-(\text{Ph})\text{C}=\text{CH}-(\text{OEt})\text{C}=\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$), e.g., **167** and **168**,



SCHEME 69. (Amino)ketocarbene complexes and acid amides.

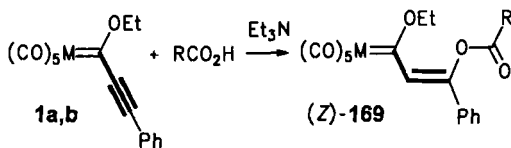


SCHEME 70. Binuclear carbene complexes of enol ether type.

are obtained from dihydroxyaryl compounds $\text{Ar}(\text{OH})_2$ (Ar = 1,4-phenylene, 1,3-phenylene, and 1,1'-binaphthyl) (Scheme 70).¹⁰³

K. 2-(Acyloxy)alkenyl Carbene Complexes

(1-Alkenyl)carbene complexes (= 2,4-dioxy-1-metalla-1,3-dienes) $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{OR}^1)\text{R}$ of chromium and tungsten have attracted much interest as C_3 building blocks for organic synthesis because of their structural relationship to β -ketoester equivalents of the enol ether (R^1 = alkyl) and enol ester types (R^1 = acyl), respectively. Compounds containing an enol ether unit are expected to react quite differently from compounds containing an enol ester moiety. [2-(Acyloxy)ethenyl]carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{OCOR})\text{Ph}$ (**Z**)-**169** (M = Cr, W; R = Ph, $p\text{-Me}_2\text{NC}_6\text{H}_4$, CH_3 , $c\text{-C}_7\text{H}_7\text{CH}_2$, $\text{PhCH}=\text{CPh}$, $\text{Me}_2\text{C}=\text{CH}$, 1,4- C_6H_4) are obtained by the addition of carboxylic acids $\text{R}-\text{CO}_2\text{H}$ to (1-alkynyl)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{C}\equiv\text{CPh}$ **1a,b** (M = Cr, W) in the presence of Et_3N at 20°C in 71–78% isolated yields (Scheme 71). The reaction is regio- and stereochemically uniform. Ligand disengagement with *t*-butylisocyanide results in the formation of 2-(acyloxy)ethenyl ketene imines $t\text{-BuN}=\text{C}=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{OCOR})\text{Ph}$ (>95% yields).¹⁶⁹ Addition of 4-aminobenzoic acid to 1 eq of (1-alkynyl)carbene complexes **1a,b** is chemoselective with respect to addition of the nitrogen atom to the $\text{C}\equiv\text{C}$



SCHEME 71. 2-(Acyloxy)ethenyl carbene complexes.

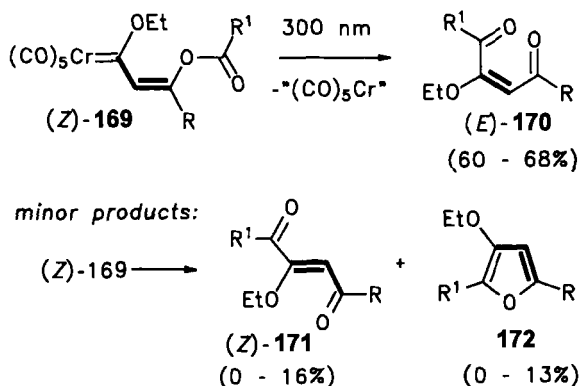
bond, whereas addition to the carboxyl group to the $C\equiv C$ bond is achieved by addition of a second equivalent of **1a,b**.

L. Butene 1,4-Diones by Photolysis of 4-Acyloxy-1-chroma-1,3-dienes

Photolysis of [(Z)-2-(acyloxy)ethenyl]carbene complexes (= 4-acyloxy-1-chroma-1,3-dienes) $(CO)_5Cr=C(OEt)-CH=C(OCOR^1)R$ (**(Z)-169** ($R = C_6H_5, t-Bu, c-Pr$; $R^1 = C_6H_5, c-Pr, c-C_7H_7CH_2, t-Bu, Me_2C=CH$) with UV light of >300 nm affords 2-butene 1,4-diones $R^1CO-C(OEt)=CH-COR$ (**(E)-170** (60–68%) by a novel metal-mediated acyl migration. Compounds (**(Z)-171** and furans **172** are formed as minor products (Scheme 72).⁴⁸

M. Thiocarbene Complexes

Fischer-type (alkylthio)- and (arylthio)carbene complexes¹⁸⁷ are available by thiolysis of the corresponding alkoxycarbene complexes in presence of a base catalyst,¹⁸⁸ or by thiolysis of (acyloxy)carbene complexes generated *in situ*.^{10c,10d,189–192} Addition of thiols R^1SH ($R^1 = \text{alkyl, aryl}$)



SCHEME 72. Butene 1,4-diones by photolysis of [2-(acyloxy)ethenyl]carbene complexes.

to (1-alkynyl)carbene complexes **1** affords Michael adducts $(\text{CO})_5\text{M}=\text{C}(\text{OEt})-\text{CH}=\text{CR}(\text{SR}^1)$ ($\text{M} = \text{Cr}, \text{W}$), which readily form $(\text{CO})_4\text{M}$ chelate complexes.^{20,173b} (1-Amino)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{NEt}_2)-\text{CMe}=\text{CR}(\text{SR}^1)$ of related structure have been prepared by insertion of an 1-amino alkyne into the $\text{M}=\text{C}$ bond of a (1-organylthio)carbene complex.^{191,193}

VI

1-ALKYNYL ACYLMETALLATES

A common route to alkoxy(1-alkynyl)carbene complexes **1** involves addition of a 1-lithio alkyne to a metal carbonyl to give an acyl metallate, which on alkylation affords an alkoxy(1-alkynyl)carbene complex (vide supra). Several transformations of acyl metallates with electrophiles other than alkylation agents have been reported.

A. Oxacyclopenten-2-ylidene Complexes by Cyclization of Acylmetallates

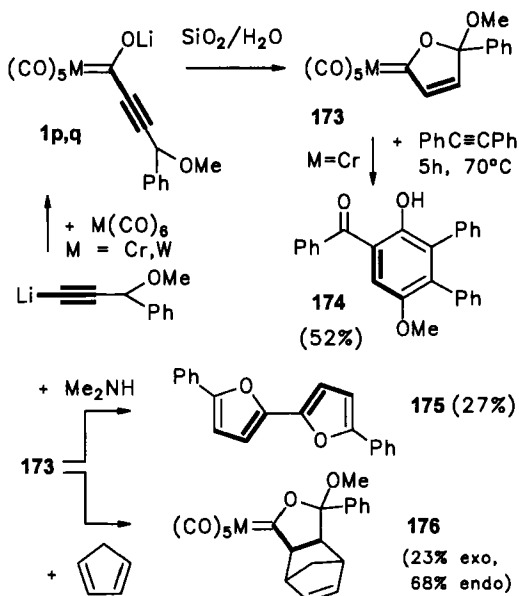
Acylmetallates **1p,q** generated by addition of lithio prop-2-ynyl ethers to hexacarbonyl chromium or tungsten afford oxacyclopenten-2-ylidene complexes **173** on contact with wet silica gel (Scheme 73).¹⁹⁴ The chromium complex **173** ($\text{M} = \text{Cr}$) undergoes a condensation with toluene to give a 1,4-dioxy aromatic compound **174**. Addition of cyclopentadiene to **173** ($\text{M} = \text{W}$) affords a Diels–Alder adduct **176** in a 1:3 exo/endo ratio,¹⁹⁵ while addition of dimethylamine quite unexpectedly does not lead to production of an aminocarbene complex but to formation of 5,5'-diphenyl-2,2'-bifuran **175** (Scheme 73).¹⁹⁶

B. Binuclear Allenylidene Complexes

Acylmetallates **1**, derived from dilithio dimethylpropargylic alcohol $\text{Li}_2[\text{C}\equiv\text{C}-\text{CMe}_2\text{O}]$ on addition of acetyl chloride, afford a 2-oxacyclopentenylidene complex **177** ($\text{M} = \text{W}$, 32%), and a dimer **178** ($\text{M} = \text{Cr}$, 36%), respectively (Scheme 74).¹⁹⁷

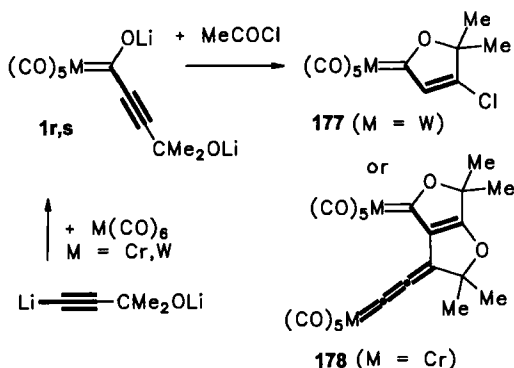
C. μ -Allenylidene Complexes

Irradiation of acylmetallates **1t,u**, derived from dilithio diphenylpropargyl alcoholate $\text{Li}_2[\text{C}\equiv\text{C}-\text{CPh}_2\text{O}]$, yields σ -alkynyl complexes **179** by extrusion

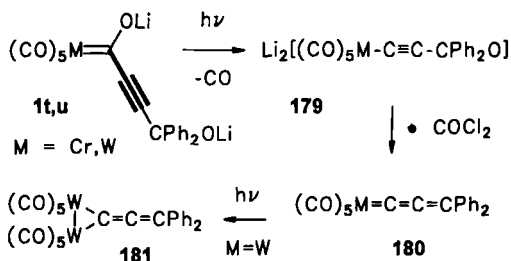


SCHEME 73. Cyclization of alkynyl acylmetallates.

of CO (Scheme 75). On addition of COCl_2 , these complexes are transformed into diphenylallenylidene complexes **180** (20–30%). The tungsten complex **180** is converted photochemically or thermally into a binuclear μ -diphenylallenylidene complex **181**.^{198,199} Allenylidene and μ -allenylidene complexes of Mn and Re, as well as those of Fe, were obtained in similar



SCHEME 74. Cyclization of alkynyl acylmetallate dianions.



SCHEME 75. Alkynyl and allenylidene complexes.

reactions.²⁰⁰ Note that generation of allenylidene complexes via acylmetalates **1t,u** affords alkyl as well as aryl derivatives, whereas allenylidene complexes with nitrogen or oxygen substituents (at the terminal carbon atom) are available, for example, by the routes given in Scheme 33 and Scheme 61, respectively. Other than via acylmetalates, formed by addition of $\text{Li}_2[\text{C}\equiv\text{C}-\text{CPh}_2\text{O}]$ to a carbonyl ligand of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr, W}$), allenylidene complexes can be also obtained by addition of $\text{Li}_2[\text{C}\equiv\text{C}-\text{CPh}_2\text{O}]$ to $(\text{CO})_5\text{M}(\text{THF})$ ($\text{M} = \text{Cr, W}$).^{126,153,199c,201,224}

VII

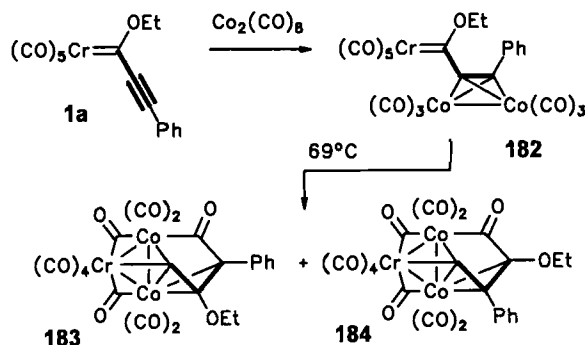
METALLATION/TRANSMETALLATION

Because of the highly unsaturated character of (1-alkynyl)carbene complexes **1**, a variety of metal π -complexes can be derived from coordination of the $\text{M}=\text{C}$ as well as of the $\text{C}\equiv\text{C}$ bonds.

A. Dicobalt Complexes of the $\text{C}\equiv\text{C}$ Bond and Isomers

Ethoxy(1-alkynyl)carbene complex **1a** forms a stable cobalt complex **182**, whose structure has been elucidated by X-ray analysis.^{145a,b} Cobalt complexes of similar type have been derived from *O*-allyl-¹⁴⁷ and *N*-allyl(1-alkynyl)carbene complexes **135** (Scheme 53).¹⁴⁵ In contrast to thermolysis of compounds **135** (Scheme 53), thermolysis of compound **182** affords isomers **183** (structure based on X-ray analysis) and **184** (structure based on spectroscopic evidence only) in 48% total yield (Scheme 76).

Reaction of diallylamino(1-alkynyl)carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{Nallyl}_2)-\text{C}\equiv\text{CR}$ ($\text{R} = \text{Cr, W}$) with $\text{Co}_2(\text{CO})_8$ affords different products, depending on the substituents R on the alkyne unit. Although formation of a cyclopentenone in 80% yield is observed in the case of $\text{R} = \text{Ph}$, $\text{M} =$

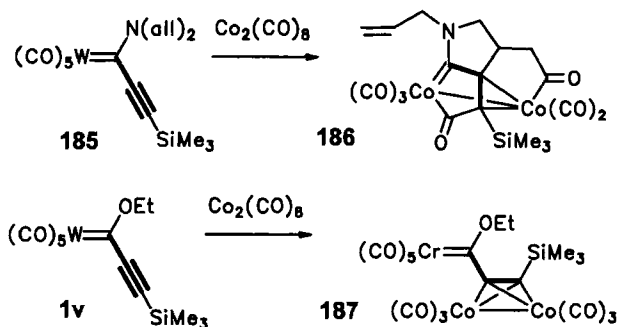


SCHEME 76. Dicobalt derivatives of alkoxy-carbene complexes.

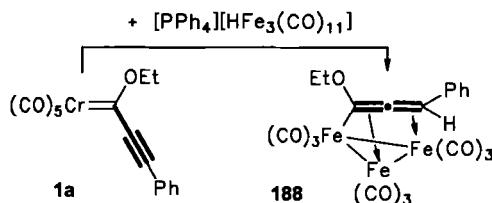
W (Scheme 53),³⁹ a transmetalation product **186** is derived in 58% overall yield from compound **185** ($\text{R} = \text{SiMe}_3$, $\text{M} = \text{W}$) (Scheme 77).²⁰² The *ethoxy* silyl(1-alkynyl) derivative **1v** forms a stable $\text{Co}_2(\text{CO})_6$ adduct **187** to the $\text{C}\equiv\text{C}$ bond, as does the corresponding phenyl complex **1b** (see Scheme 53).^{144a}

B. Trinuclear Allenyl Iron Complexes

A stable trinuclear iron cluster **188** in which an allenyl unit is bonded in a $\mu^3-\eta^3$ fashion has been derived from compound **1a** by transmetalation



SCHEME 77. Dicobalt derivatives of aminocarbyne complexes.



SCHEME 78. Trinuclear iron derivative of an alkoxy(1-alkynyl)carbene complex.

with $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{13}]$ (Scheme 78).²⁰³ Note that addition of the $\text{Fe}-\text{H}$ bond to the (1-alkynyl)carbene ligand is of regiochemistry opposite to that of $\text{Bu}_3\text{Sn}-\text{H}$ (Scheme 31).

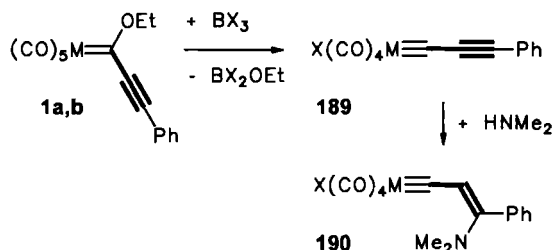
VIII

1,2-ELIMINATION WITH FORMATION OF ALKYNYL CARBYNE COMPLEXES

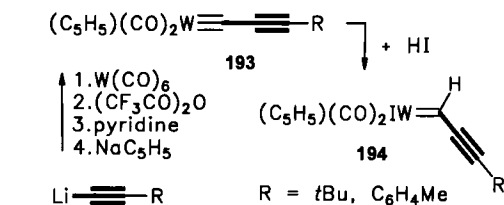
Fischer carbyne complexes are usually generated from carbene complexes by 1,2-elimination of an alcohol under the influence of boron trihalides²⁰⁴ or other Lewis acids.²⁰⁵

A. 4-Amino-1-metalla-1-yne-3-ene

Following the Fischer procedure, alkynyl carbyne complexes *trans*- $\text{X}(\text{CO})_4\text{M}\equiv\text{C}-\text{C}\equiv\text{CPh}$ **189** have been obtained in 30–60% yields by reaction of (1-alkynyl)carbene complexes **1a,b** ($\text{M} = \text{Cr}, \text{W}$) with BX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). To date, (1-alkynyl)carbyne compounds have found application as catalysts as well as stoichiometric reagents in organic synthesis.^{205c,206} Among the transformations reported thus far is the formation of a 4-amino-1-metalla-1-yne-3-ene (= enamino carbyne complex) **190** by addition of HNMe_2 to compound **189** (Scheme 79).²⁰⁷



SCHEME 79. 4-Amino-1-metalla-1-yne-3-enes.

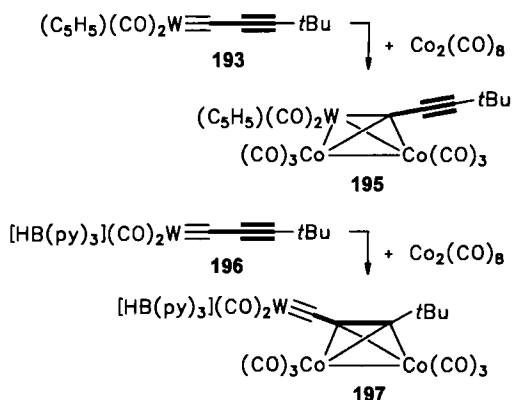


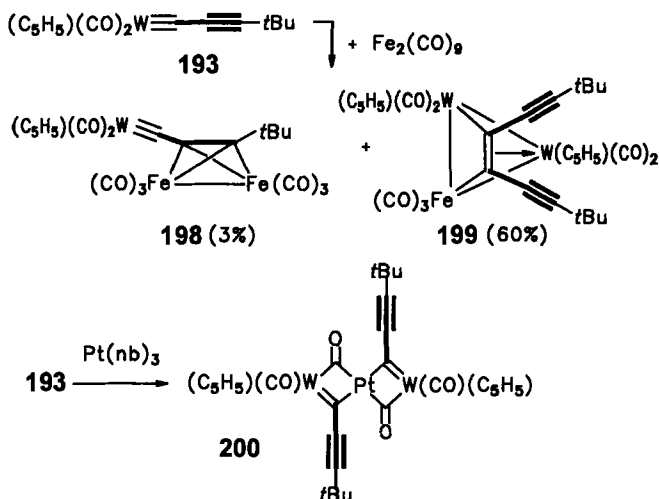
SCHEME 81. Schrock-type (1-alkynyl)carbene complexes.

yl)hydroborate} affords neutral complexes of the type $L(CO)_2W \equiv C-C \equiv C(t-Bu)$. Addition of HI to compounds **193** gives Schrock-type hydrido(1-alkynyl)carbene complexes **194** (34%, $R = Ar$; 57%, $R = t-Bu$) in which the hydrogen atom is attached to the carbene carbon atom (Scheme 81).²¹⁶

D. Selective Metallation of $M \equiv C$ and $C \equiv C$ Bonds of Carbyne Complexes

(1-Alkynyl)carbyne complexes contain two potentially active sites, the $M \equiv C$ and the $C \equiv C$ bonds, for combination with further metal moieties to generate di-, tri-, and polynuclear mixed-metal complexes. Metallation of the triple bonds was found to be highly selective. Thus, $(\eta^5-C_5H_5)(CO)_2W \equiv C-C \equiv C(t-Bu)$ **193** forms compound **195** in quantitative yield by chemoselective addition of $Co_2(CO)_8$ to the $M \equiv C$ bond, with no evidence for addition at the $C \equiv C$ bond, whereas formation of an adduct **197** to the $C \equiv C$ bond is observed as the only product derived from the boranate compound **196** (Scheme 82).²¹⁴

SCHEME 82. Selective metallation of $M \equiv C$ and $C \equiv C$ bonds of carbyne complexes.



SCHEME 83. Metallation of carbyne complexes with concomitant ligand dimerization.

E. Metallation of Carbyne Complexes with Concomitant Ligand Dimerization

Reaction of compounds **193** and **196** with $\text{Mo}_2(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)_2$ affords products with structures analogous to those obtained with $\text{Co}_2(\text{CO})_8$. Reaction of compound **193** with $\text{Fe}_2(\text{CO})_9$ gives two products, compound **198**, derived from metallation of the $\text{C}\equiv\text{C}$ bond, and compound **199**, resulting from metallation of the $\text{W}\equiv\text{C}$ bond with concomitant dimerization of the ligand (Scheme 83).²¹⁷

F. Mixed-Metal Clusters Derived from (1-Alkynyl)carbyne Complexes

Mono and bis metallation of the $\text{M}\equiv\text{C}$ bond of **193**, as well as of the corresponding molybdenum complex, also has been achieved with $\text{Rh}(\text{CO})_2(\eta^5\text{-indenyl})$, whereas a bridged platinum complex **200** is obtained in 83% yield on metallation of **193** with $\text{Pt}(\text{norbornene})_3$ (Scheme 83).²¹⁸ Many formally related transformations based on the isolobal relationship between $\text{M}\equiv\text{C}$ and $\text{C}\equiv\text{C}$ bonds have been carried out. Thus, metallation of $[\text{NEt}_4][(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)(\text{CO})\text{W}\equiv\text{C}-\text{C}\equiv\text{CR}]$ with excess $\text{Fe}_2(\text{CO})_9$ affords an anionic WFe_2 cluster $[\text{NEt}_4][(\eta^5\text{-C}_2\text{B}_9\text{H}_8\text{Me}_2)(\text{CO})_8\text{WFe}_2\{\mu_3\text{-}\eta^3, \eta^5\text{-CH}=\text{C}=\text{C}(t\text{-Bu})-\text{C}(\text{OH})\}]$ in 40% yield,²¹⁹ whereas metallation with $(\text{CO})_3\text{Mo}(\text{MeCN})_3$ gives a trimetallic WMo_2 compound.²²⁰ A great diversity of mixed clusters is obtained by metal-exchange reactions. For example, it has been shown that the last-named compound reacts with $[\text{Au}(\text{PPh}_3)]^+$

[generated *in situ* from $\text{AuCl}(\text{PPh}_3)$ and TiPF_6] with formation of a binuclear WAu complex $(\eta^5\text{-C}_2\text{B}_9\text{H}_8\text{Me}_2)(\text{CO})_2\text{WAu}[\mu_2\text{-C}-\text{C}\equiv\text{C}(t\text{-Bu})]$, which may formally considered to be a (1-auro)(1-alkynyl)carbene complex. Treatment of $[\text{NEt}_4][(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)(\text{CO})_2\text{W}\equiv\text{C}-\text{C}\equiv\text{C}(t\text{-Bu})]$ with 1 eq CuCl or $\text{AuCl}(\text{tht})$ (tht = tetrahydrothiophene) affords labile adducts $[\text{NEt}_4][(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)(\text{CO})_2\text{WMCl}\{\mu\text{-C}-\text{C}\equiv\text{C}(t\text{-Bu})\}]$ ($\text{M} = \text{Cu}, \text{Au}$), whereas a stable WCu_2 complex $[\text{NEt}_4][(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)(\text{CO})_2\text{WCu}_2\text{Cl}_2\{\mu_3\text{-C}-\text{C}\equiv\text{C}(t\text{-Bu})\}]$ is formed on addition of 2 eq of CuCl instead of 1 eq.²²⁰ For related transformations of (1-alkynyl)carbyne cluster compounds, see Ref.²²¹

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Chalcogen-Bridged Metal–Carbonyl Complexes

PRADEEP MATHUR

*Chemistry Department
Indian Institute of Technology
Powai, Bombay 400 076, India*

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I

INTRODUCTION

Incorporation of ligands derived from certain main-group elements has become an area of considerable investigation. The Group 16 elements have been among the most widely used for the purpose of bridging different metal fragments in cluster-growth reactions. The chemistry of transition-metal–chalcogenide clusters has been widely explored because of their theoretical and structural interest, as well as their involvement in several fields.^{1–5} Although the sulfido ligand has been widely used in systematic syntheses of clusters, the use of Se and Te in this respect is recent and relatively less well studied, probably because it has been assumed that the heavier congeners of S would behave in a similar fashion in their ability to bridge and stabilize metal frameworks, and secondly because of a belief that the metal selenides and tellurides would have the high level of toxicity and unpleasant odor that one generally associates with organoselenides and organotellurides. Work on the Se- and Te-containing complexes shows that in many cases Se-bridged metal complexes are more closely related

to the sulfur analogs; the large tellurium atom imparts some unusual features to its metal complexes. Recent investigations show that in some clusters, the behavior of selenium can be different from that of both sulfur and tellurium. Diversity in structure and reactivity features of chalcogen-bridged metal complexes has generated interest in the synthesis of new chalcogen-bridged complexes and study of their reactions toward inorganic and organic moieties.

Many reviews have covered the chemistry of transition-metal, main-group compounds,⁵⁻¹² and because the title subject is too vast to be covered fully in this review, emphasis will be given to complexes containing selenium and tellurium; reference to compounds containing sulfur will be included for purposes of comparison.

II

CATIONIC CLUSTERS

The cations Se_4^{2+} , Te_6^{4+} , S_8^{2+} , Se_8^{2+} , and S_{19}^{2+} are well known and have been the subjects of considerable structural and spectroscopic study.¹³⁻¹⁷ The reactions of $\text{Se}_4(\text{AsF}_6)_2$, $\text{Se}_8(\text{AsF}_6)_2$, and $\text{Se}_{10}(\text{SbF}_6)_2$ with $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ in liquid SO_2 form the diamagnetic complexes $[\text{M}_2(\text{CO})_{10}\text{Se}_4][\text{EF}_6]_2$ ($\text{M} = \text{Mo}$, $\text{E} = \text{As}$ (1), Sb (2); $\text{M} = \text{W}$, $\text{E} = \text{As}$ (3), Sb (4)). The structure of 3 (Fig. 1) has been established by X-ray crystallography. Its structure consists of two centrosymmetrically related pentagonal-bipyramidal $\text{W}(\text{CO})_5(\eta^2\text{-Se}_2)^+$ groups linked by weak Se—Se

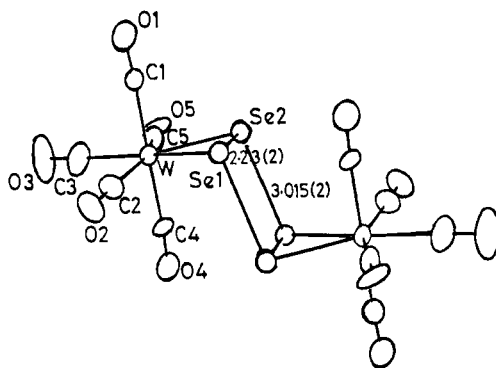


FIG. 1. Molecular structure of $[\text{W}_2(\text{CO})_{10}\text{Se}_4][\text{AsF}_6]_2$ (3). [Reprinted with permission from Collins, M. J.; Gillespie, R. J.; Kolis, J. W.; Sawyer, J. F. *Inorg. Chem.* **1986**, 25, 2057. Copyright 1986 American Chemical Society.]

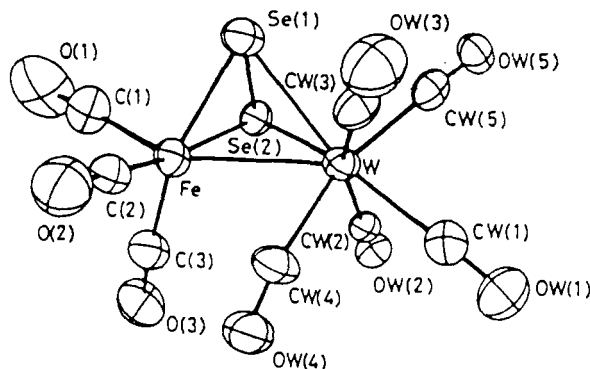


FIG. 2. Molecular structure of $[\text{FeW}(\text{Se}_2)(\text{CO})_8][\text{SbF}_6]_2$ (5). [Reprinted with permission from Seigneurine, A.; Makani, T.; Jones, D. J.; Roziere, J. *J. Chem. Soc., Dalton Trans.* **1987**, 2111. Copyright 1987 Royal Society of Chemistry.]

bonds of length $3.015(2)$ Å between the diselenide groups. The Se–Se distance in the $\eta^2\text{-Se}_2$ moiety is $2.213(2)$ Å. The $\eta^2\text{-Se}_2^+$ group appears to exert a significant *trans* influence; the CO bond *trans* to the Se_2 group is the shortest of the five CO bonds. The *trans* CO also has the longest W–C bond, and it is implied that the Se_2^+ group is a fairly good σ -donor as well as a good π -acceptor.^{18,19}

The square S_4^{2+} , Se_4^{2+} , and Te_4^{2+} species have delocalized π -orbitals containing six electrons, and therefore there has been some investigation of the possibility that these cations might react with transition-metal–carbonyl

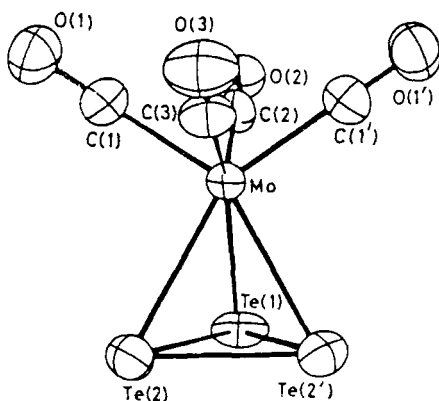
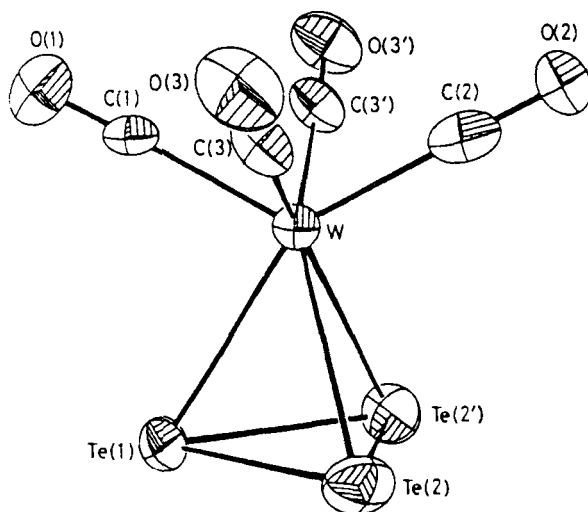


FIG. 3. Molecular structure of $[\text{Mo}(\text{Te}_3)(\text{CO})_4][\text{SbF}_6]_2$ (6). [Reprinted with permission from Seigneurine, A.; Makani, T.; Jones, D. J.; Roziere, J. *J. Chem. Soc., Dalton Trans.* **1987**, 2111. Copyright 1987 Royal Society of Chemistry.]



complexes to form six- π -electron-donor complexes. Tetrahedrane-like dicationic clusters, $[\text{FeW}(\text{Se}_2)(\text{CO})_8][\text{SbF}_6]_2$ (**5**) (Fig. 2) and $[\text{Mo}(\text{Te}_3)(\text{CO})_4][\text{SbF}_6]_2$ (**6**) (Fig. 3), have been prepared by reaction of the metal carbonyls $\text{Fe}_2(\text{CO})_9$, $\text{W}(\text{CO})_6$, and $\text{Mo}(\text{CO})_6$ with the homonuclear cations Se_4^{2+} and Te_4^{2+} .^{20,21} The tungsten compound $[\text{W}(\text{Te}_3)(\text{CO})_4][\text{SbF}_6]_2$ (**7**) (Fig. 4) has been prepared by the reaction of $\text{W}(\text{CO})_6$ with $\text{Te}_4(\text{SbF}_6)_2$.²²

The FeW(Se₂) core of **5** adopts a distorted tetrahedral arrangement. The selenium fragment in the cluster may formally be considered as an Se₂²⁺ ion stabilized by organometallic groups. The Se–Se bond length, 2.281(3) Å, corresponds to an approximate Se–Se bond order of 1.5,²³ indicating the presence of extensive delocalization.

The structural features of **6** and **7** are almost identical. The overall structure of both can be described as “piano-stool” geometry with the metal-tetracarbonyl fragment possessing C_{4v} symmetry and the Te_3^{2+} ring having C_{3v} symmetry.

When the polysulfur and selenium cationic clusters S_8^{2+} and Se_8^{2+} are reacted with $Fe(CO)_5$ or $Fe_2(CO)_9$, different iron carbonyl cluster cations are isolated depending on the nature of the counteranion used. With SbF_6^- as the counteranion, $[Fe_3(E_2)_2(CO)_{10}][SbF_6]_2SO_2$ ($E = S$ (**8**), Se (**9**)) is isolated from the reaction of E_8^{2+} and iron carbonyl. The structure of **9** (Fig. 5) has been established by X-ray methods. The cluster cation consists

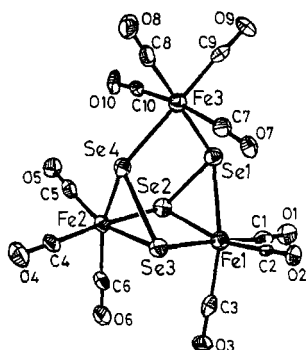


FIG. 5. Molecular structure of $[\text{Fe}_3(\text{Se}_2)_2(\text{CO})_{10}][\text{SbF}_6]_2\text{SO}_2$ (**9**). [Reprinted with kind permission from Drake, G. W.; Schimek, G. L.; Kolis, J. W. The coordination chemistry of cationic main group clusters: Syntheses and structures of $[\text{Fe}_3(\text{Se}_2)_2(\text{CO})_{10}]^{2+}$ and $\text{Fe}_4(\text{Se}_2)_3(\text{CO})_{12}^{2+}$. *Inorg. Chim. Acta* **1995**, 240, 63. Copyright 1995 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

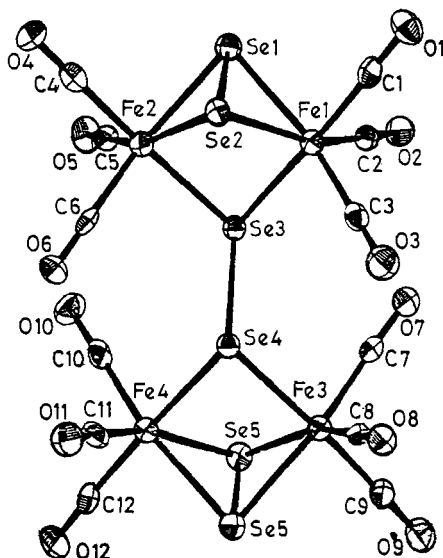


FIG. 6. Molecular structure of $[\text{Fe}_4(\text{Se}_2)_3(\text{CO})_{12}][\text{SbF}_6]_23\text{SO}_2$ (**11**). [Reprinted with kind permission from Drake, G. W.; Schimek, G. L.; Kolis, J. W. The coordination chemistry of cationic main group clusters: Syntheses and structures of $[\text{Fe}_3(\text{Se}_2)_2(\text{CO})_{10}]^{2+}$ and $\text{Fe}_4(\text{Se}_2)_3(\text{CO})_{12}^{2+}$. *Inorg. Chim. Acta* **1995**, 240, 63. Copyright 1995 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

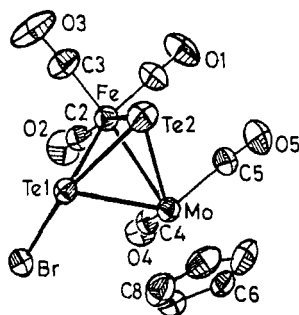


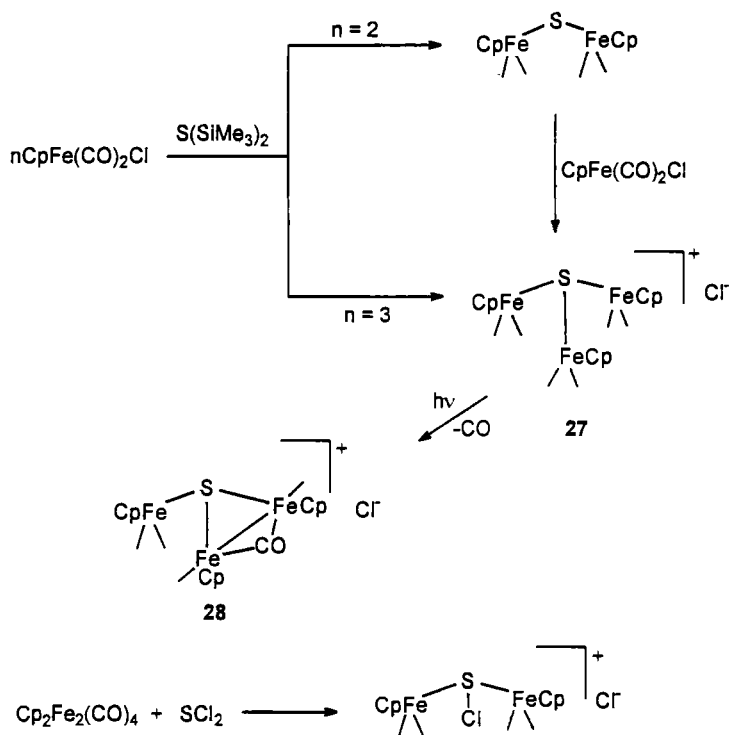
FIG. 7. Molecular structure of $[(C_5H_5)MoFeTe_2Br(CO)_5]$ (**16**). [Reprinted with permission from Bogan, L. E. Jr.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1985**, *24*, 3722. Copyright 1985 American Chemical Society.]

of a “picnic-basket” arrangement of two $Fe(CO)_3$ groups linked by two Se_2 groups and the whole fragment capped by an $Fe(CO)_4$ group.

On the basis of similarities in the carbonyl stretching patterns, the S-analog is thought to have an identical structure to that of the Se-cation. In spectra of both compounds, there is a large shift of C–O stretching frequencies to higher values as compared with those of $Fe(CO)_5$, suggesting that the iron centers are very electron poor, and there is substantial loss of electron density in the π -back-bonding orbitals between the iron atoms and the carbonyl groups. This is also evident from the lengthened Fe–C and shortened C–O bond distances. When $Sb_2F_{11}^-$ is used as the counteranion, the cationic clusters $[Fe_4(E_2)_3(CO)_{12}][SbF_6]_2 \cdot 3SO_2$ ($E = S$ (**10**), Se (**11**)) are obtained, with the S-compound being formed in smaller amount than the Se-cluster cation. Although $Sb_2F_{11}^-$ is used, the only counterion isolated in either case is SbF_6^- . The structure of **11** (Fig. 6) has been determined by X-ray methods.²⁴

The reaction of $[S_8][AsF_6]_2$ with $Co_2(CO)_8$ in the presence of SO_2 forms the dicobalt cationic complex $[Co_2(CO)_6(\mu-S_2)][AsF_6]SO_2$ (**12**). It has been structurally characterized crystallographically and shows a Co_2S_2 four-membered ring, like the ones in $Fe_2E_2(CO)_6$ complexes, with an S–S bond distance of $1.98(2) \text{ \AA}$.²⁵

Bromination of $(RC_5H_4)_2Mo_2FeTe_2(CO)_7$ ($R = H, Me, i\text{-}Pr$) forms $(RC_5H_4)Mo(CO)_3Br$ (**13–15**) and $(RC_5H_4)MoFeTe_2Br(CO)_5$ (**16–18**). The structure of **16** (Fig. 7) consists of a $MoFeTe_2$ tetrahedral core with Br atom attached to one Te atom. A Te–Te–Br angle of 120° indicates the presence of a stereochemically active lone pair at the four-coordinate Te center.



SCHEME 1.

The cationic species $[(\text{RC}_5\text{H}_4)\text{MoFe}(\text{Te}_2)(\text{CO})_5][\text{SbF}_6]$ (**17**), thought to be an intermediate in a dynamic process observed in the variable-temperature ^1H NMR study of **16–18**, can be made quantitatively from the reaction of **16–18** with AgSbF_6 . Reduction of $[(\text{RC}_5\text{H}_4)\text{MoFe}(\text{Te}_2)(\text{CO})_5][\text{SbF}_6]$ with sodium borohydride yields blue diamagnetic compounds that can be analyzed to be $[(\text{RC}_5\text{H}_4)\text{MoFe}(\text{Te}_2)(\text{CO})_5]_n$ (**19–21**) and that undergo mild bromination to give $[(\text{RC}_5\text{H}_4)\text{MoFe}(\text{Te}_2)\text{Br}(\text{CO})_5]$ (**22–25**).²⁶

The reaction of $[\text{CpFe}(\text{CO})_2\text{Cl}]$ with $\text{S}(\text{SiMe}_3)_2$ forms the diferrirosulfane, $[\{\text{CpFe}(\text{CO})_2\}_2(\mu\text{-S})]$ (**26**) (Scheme 1). The nucleophilicity of the bridging sulfur atom is established by the addition of the electrophilic complex cation $[\text{CpFe}(\text{CO})_2]^+$ to form the trinuclear complex $[\{\text{CpFe}(\text{CO})_2\}_3(\mu\text{-S})]\text{Cl}$ (**27**), which can also be prepared by the reaction of $\text{S}(\text{SiMe}_3)_2$ with an excess of $\text{CpFe}(\text{CO})_2\text{Cl}$. The triferrirosulfonium salt **27** decarbonylates on photolysis and gives $[\text{Cp}_3\text{Fe}_3(\text{CO})_4(\mu\text{-CO})(\mu_3\text{-S})]\text{Cl}$ (**28**). The reaction of $[\text{CpFe}(\text{CO})_2]_2$ with the sulfur chlorides SCl_2 or SOCl_2 leads to the formation of ionic S-functionalized species. The sulfur-containing fragments

SOCl or SOCl insert into the Fe–Fe bond to give the chlorosubstituted diferrirosulfonium or diferrirosulfoxonium salts $[\{\text{CpFe}(\text{CO})_2\}_2\text{SCI}]\text{Cl}$ (**29**) or $[\{\text{CpFe}(\text{CO})_2\}_2\text{S}(\text{O})\text{Cl}]\text{Cl}$ (**30**).²⁷

III

ANIONIC CLUSTERS

Several approaches have been used for the synthesis of metal carbonyl polychalcogenide anions.^{28–31}

A. Hydro(solvo) Thermal Preparations

An important synthetic development has been the emergence of the hydro(solvo) thermal technique as a convenient route to metal–carbonyl polychalcogenide anions. The hydro(solvo) thermal technique has been used successfully for the synthesis of several metal carbonyl telluride clusters. Mixed-metal carbonyl telluride clusters $[\text{Ph}_4\text{P}]_2[\text{Fe}_2\text{MTe}_3(\text{CO})_{11}]$ ($\text{M} = \text{Mo}$ (**31**) (Fig. 8), W (**32**)) and $[\text{Na}(\text{Et}_4\text{N})_2][\text{Fe}_3\text{W}_2\text{Te}_8(\text{TeMe})(\text{CO})_{12}] \cdot 2\text{H}_2\text{O}$ (**33**) (Fig. 9) have been synthesized methanothermally at 80°C using mixtures of $\text{Fe}_3(\text{CO})_{12}$, $\text{M}(\text{CO})_6$ ($\text{M} = \text{Mo}, \text{W}$), and Na_2Te_2 with Ph_4PBr or $\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}$ in a sealed Pyrex tube.³²

The structure of **33** can be regarded as an example of a hybrid between two homometallic structures, $[\text{Fe}_4\text{Te}_6(\text{TeMe})_2(\text{CO})_8]^{2-}$ (**34**)³³ and $[\text{W}_6\text{Te}_8(\text{CO})_{18}]^{2-}$ (**35**)³¹ (Scheme 2).

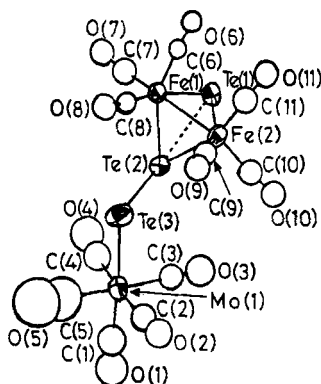


FIG. 8. Molecular structure of $[\text{PPh}_4]_2[\text{Fe}_2\text{MoTe}_3(\text{CO})_{11}]$ (**31**). [Reprinted with permission from Das, B. K.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 5721. Copyright 1995 American Chemical Society.]

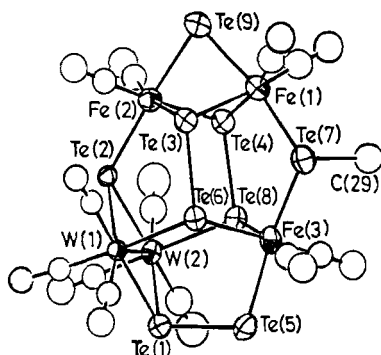
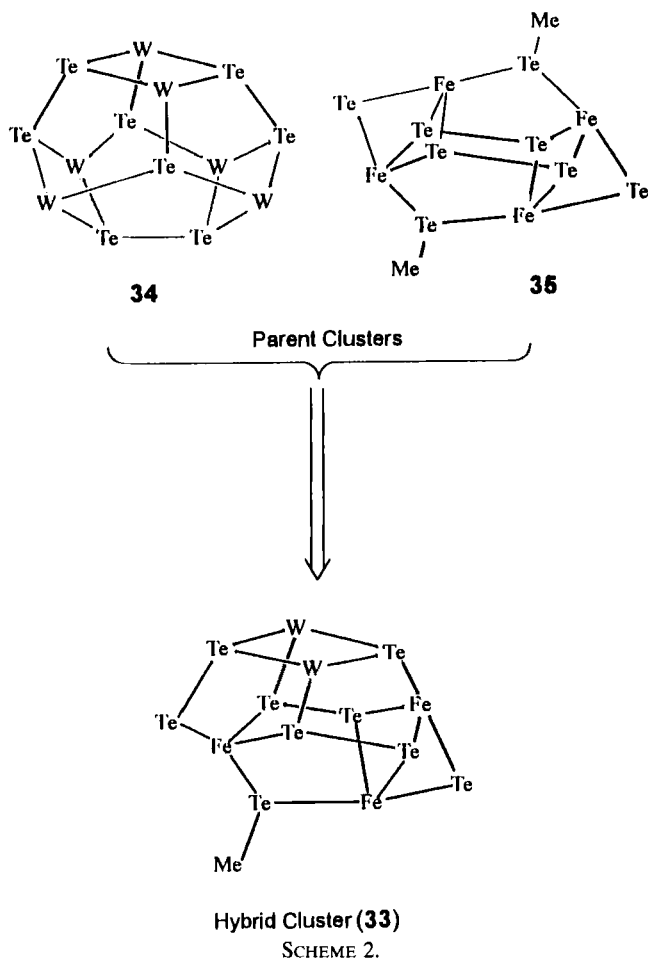


FIG. 9. Molecular structure of $[\text{Na}(\text{Et}_4\text{N})_2][\text{Fe}_3\text{W}_2\text{Te}_8(\text{TeMe})(\text{CO})_{12}]\cdot 2\text{H}_2\text{O}$ (**33**). [Reprinted with permission from Das, B. K.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 5721. Copyright 1995 American Chemical Society.]

The hexaruthenium dianionic cluster $[\text{Ph}_4\text{P}]_2[\text{Ru}_6(\text{Te}_2)_7(\text{CO})_{12}]$ (**36**) (Fig. 10) has been obtained by heating $\text{Ru}_3(\text{CO})_{12}$ with Na_2Te_2 and $\text{Ph}_4\text{P}\text{Cl}$ in H_2O at 110°C in a sealed Pyrex tube.

The structure of **36** bears a strong resemblance to that of its solid-state homolog RuTe_2 . **36** can be viewed as an intercepted cluster on the way to RuTe_2 , which forms at higher temperatures.³⁴ This is an important comparison because clusters can be considered as intermediates between molecules and solids, and therefore any structural similarities between the intermediates and the ultimate inorganic solid should be visible if such clusters can be obtained.^{35,36} Using a small volume of methanol as solvent, $[\text{Me}_4\text{N}]_2[\text{Fe}_4(\text{Te}_2)_2(\text{Te})_2(\text{TeMe})_2(\text{CO})_8]$ (**37**) is made at 110°C by reacting $\text{Fe}_3(\text{CO})_{12}$ with Na_2Te_2 and Me_4NBr in a sealed tube. The compound $[\text{Ph}_4\text{P}]_2[\text{Ru}_4(\text{Te}_2)_2(\text{Te})_2(\text{TeMe})_2(\text{CO})_8]$ (**38**) forms similarly at 80 – 130°C from $\text{Ru}_3(\text{CO})_{12}$, Na_2Te_2 , and Ph_4PBr . The anions in both compounds have the same structure (Fig. 11).

The structural motif of the $[\text{Fe}_4(\text{Te}_2)_2(\text{Te})_2(\text{TeMe})_2(\text{CO})_8]$ anion can be thought of as originating from the fusion of two $[\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$ anions.³⁰ In $[\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$ the metal atoms are held together by $\mu_2\text{-Te}^-$ and $\mu_2, \eta^1\text{-Te}_2^{2-}$ ligands. The two dimeric anions approach each other in a centrosymmetric fashion so that the pendant tellurium atom belonging to the ditelluride ligand of one $[\text{Fe}_2\text{Te}_3(\text{CO})_6]^{2-}$ anion forms two new Fe–Te bonds with the Fe atoms of the other anion, transferring the ditelluride to a $\mu_2, \mu_2^-, \eta^1, \eta^1\text{-Te}_2^{2-}$ ligand. This proposal is supported by the fact that $[\text{Ph}_4\text{P}]_2[\text{Fe}_2\text{Te}_3(\text{CO})_6]$ (**39**) is observed in the early stages of these reactions. Also, upon heating in MeOH with Na_2Te_2 at 110°C , **39** is converted to **37**, further supporting its role as an intermediate in



the formation of the tetramers. The source of the methyl groups in the methylation of the Te^{2-} anion, which gives rise to Me-Te ligands, appears to be methanol, because hydrothermal reactions of $\text{Fe}(\text{CO})_5$ as well as of $\text{Ru}_3(\text{CO})_{12}$ with Na_2Te_2 , under the same conditions that provide **37** in MeOH , yield $[\text{Fe}_6(\text{Te}_2)_7(\text{CO})_{12}]^{2-}$ (**40**). When the reaction is carried out in ethanol, $[\text{Ph}_4\text{P}]_2[\text{Fe}_4(\text{Te}_2)_2(\text{Te})_2(\text{TeEt})_2(\text{CO})_8]$ (**41**) is isolated.³³

Formation of a thioarsenide from the reductive coupling of dithionite and arsenite under hydrothermal conditions is observed. Using $\text{Fe}_3(\text{CO})_{12}$, NaAsO_2 , $\text{Na}_2\text{S}_2\text{O}_4$, and Ph_4PBR in a 1 : 3 : 6 : 3 molar ratio in a hydrothermal reaction yields $[(\text{Ph}_4\text{P})][(\text{CO})_6\text{Fe}_2\text{AsS}]$ (**42**) (Fig. 12).³⁷

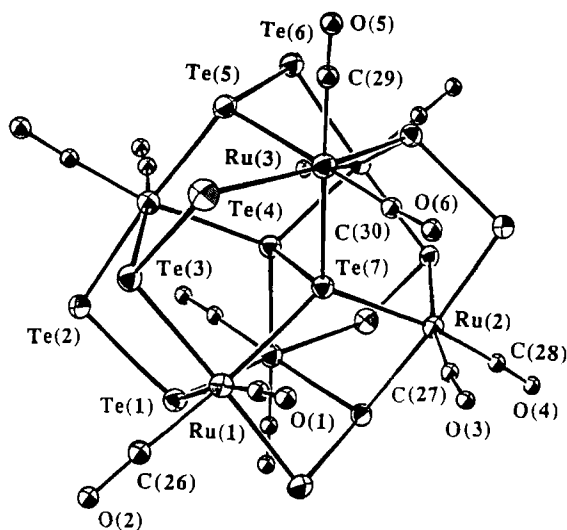


FIG. 10. Molecular structure of $[\text{PPh}_4]_2[\text{Ru}_6(\text{Te}_2)_7(\text{CO})_{12}]$ (**36**). [Reprinted with permission from Huang, S. P.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 5477. Copyright 1992 American Chemical Society.]

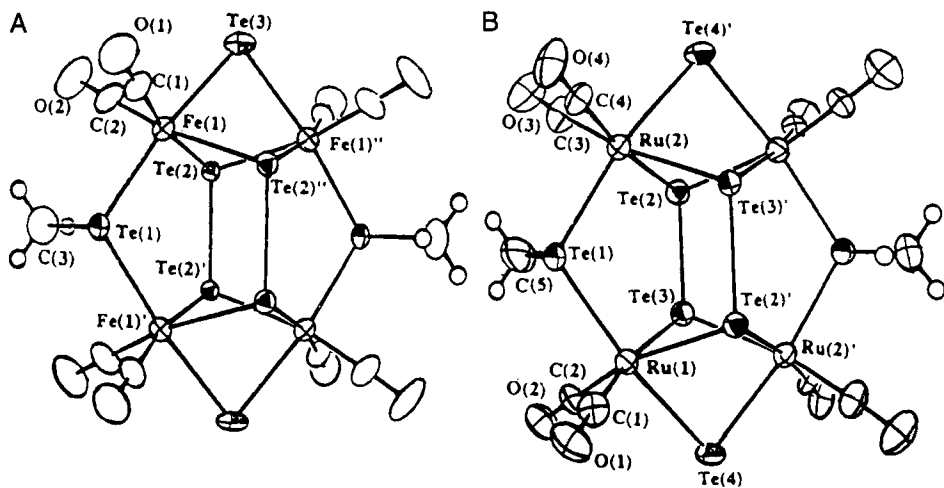


FIG. 11. Molecular structure of $[\text{Me}_4\text{N}]_2[\text{Fe}_4(\text{Te}_2)_2(\text{Te})_2(\text{TeMe})_2(\text{CO})_8]$ and $[\text{PPh}_4]_2[\text{Ru}_4(\text{Te}_2)_2(\text{Te})_2(\text{TeMe})_2(\text{CO})_8]$ (**37**, **38**). [Reprinted with permission from Das, B. K.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 1011. Copyright 1995 American Chemical Society.]

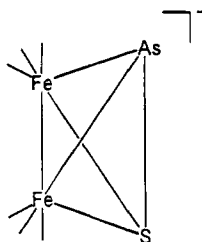


FIG. 12. Structure of $[(\text{Ph}_4\text{P})][(\text{CO})_6\text{Fe}_2\text{AsS}]$ (**42**).

B. Synthesis Using Polyanions

It has been shown that soluble main-group polyanions can be used to form metallized polymers³⁸ and metastable solids with tunable conductivities.^{39,40} As an extension of this work, there has been interest in investigating the structures and properties of transition-metal main-group polyanions, as well as their utility in forming new metastable materials.^{41,42} Steigerwald has reported the convenient low-temperature synthesis of FeTe (**43**) and FeTe_2 (**44**) from $[\text{Cp}(\text{Et}_3\text{P})(\text{CO})\text{Fe}]\text{Te}_n$ (**45**) compounds.⁴³

The reaction of polychalcogenides with transition-metal carbonyls to give a variety of novel products occurs by an internal redox mechanism.⁴⁴ Electrons are transferred from the zero-valent metal center to the polychalcogenide ion, resulting in the oxidative decarbonylation of the metal and reductive cleavage of the chalcogenide chain. Polysulfides and polyselenides can induce complete oxidative decarbonylation, producing high-valent metal centers.^{45,46}

On the other hand, polytellurides only seem to oxidize metals to the +I or +II state. Reaction of equimolar amounts of Te_4^{2-} with $\text{M}(\text{CO})_6$ results in disubstitution of CO forming a *cis*-complex $(\text{CO})_4\text{MTe}_4$ ($\text{M} = \text{Cr}$ (**45**), W (**47**)).⁴⁷ If an excess of metal carbonyl is used in the presence of polytelluride anion, multinuclear products can be isolated and metal-metal bonds can also form, leading to clusters. Careful manipulation of reaction conditions and choice of the polychalcogenide anion used makes possible partial oxidation of the metal centers and cluster formation. The reaction of iron carbonyls with polytelluride anions can lead to a wide array of cluster compounds, the identities of which are controlled by the stoichiometries and compositions of the starting telluride anions. For instance, reaction of $[\text{Fe}(\text{CO})_5]$ with Te^{2-} leads to the formation of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-Te})]^{2-}$ (**48**),⁴⁸ whereas its reaction with increasing amounts

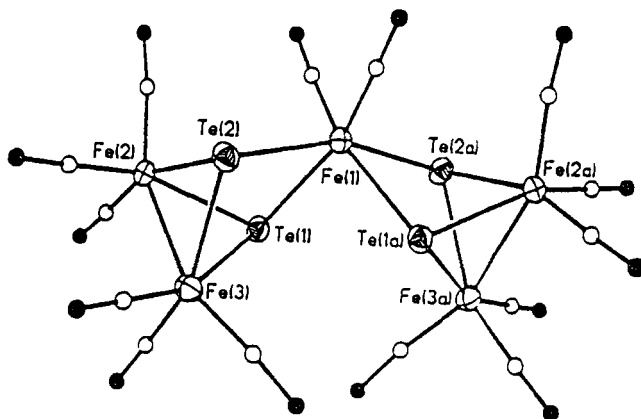


FIG. 13. Molecular structure of $[\text{Fe}_5(\text{CO})_{14}\text{Te}_4]^{2-}$ (**49**). [Reprinted with permission from Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 913. Copyright 1992 VCH Publications.]

of Te_4^{2-} yields $[\text{Fe}_5(\text{CO})_{14}\text{Te}_4]^{2-}$ (**49**) (Fig. 13),⁴⁹ $[\text{Fe}_6(\text{CO})_{16}\text{Te}_6]^{2-}$ (**50**),⁵ and $[\text{Fe}_8(\text{CO})_{20}\text{Te}_{10}]^{2-}$ (**51**) (Fig. 14),⁴⁹ successively.

Related investigations on polysulfide and polyselenide anions with iron carbonyl reveal that there is an equally rich chemistry of sulfides and selenides, but it is substantially different from that of the tellurides. For instance, attempts to obtain lighter analogs of **51** under similar

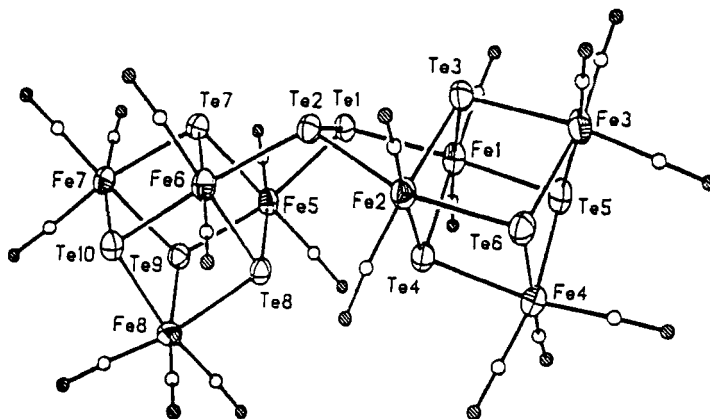


FIG. 14. Molecular structure of $[\text{Fe}_8(\text{CO})_{20}\text{Te}_{10}]^{2-}$ (**51**). [Reprinted with permission from Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 913. Copyright 1992 VCH Publications.]

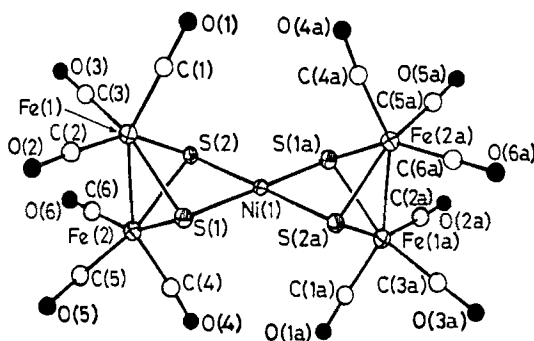
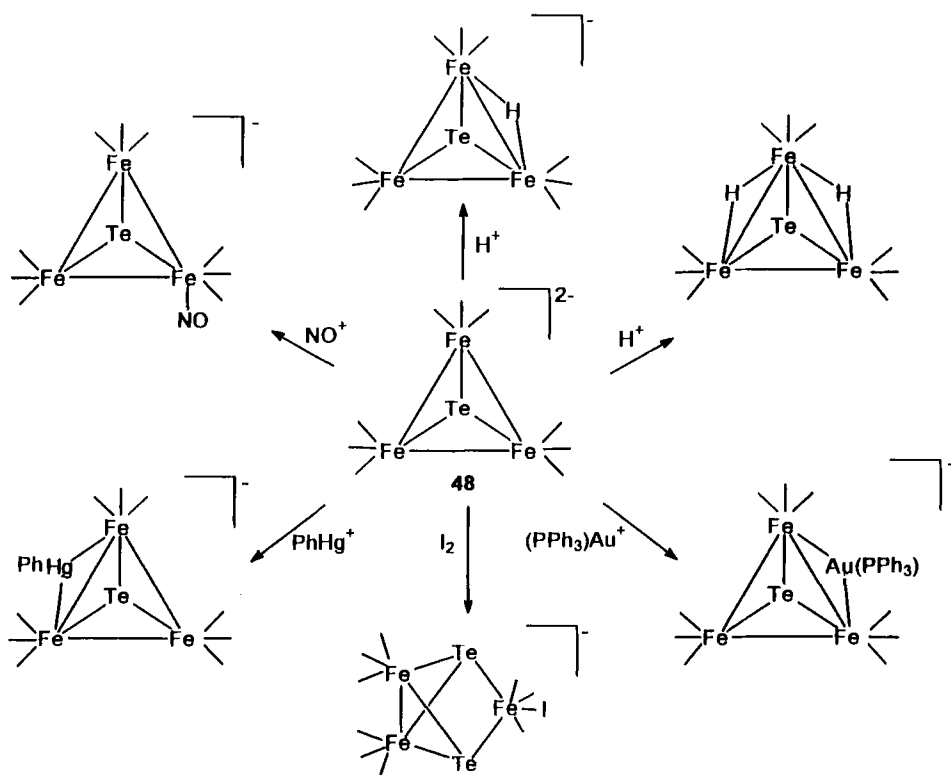


FIG. 15. Molecular structure of $[\text{PPh}_4]_2[\{\text{Fe}_2(\text{CO})_6(\mu_3\text{-S})_2\}\text{Ni}]$ (**57**). [Reprinted with permission from Holliday, R. L.; Roof, L. C.; Hargus, B.; Smith, D. M.; Wood, P. T.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1995**, *34*, 4392. Copyright 1995 American Chemical Society.]

conditions have been unsuccessful. The reaction of excess iron carbonyl with almost any polysulfide or selenide eventually leads to the formation of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})]^{2-}$ ($\text{E} = \text{S}$ (**52**), Se (**53**)). When E_2^{2-} is used, $[\text{Fe}_5(\text{CO})_{14}(\mu_3\text{-E})_2]^{2-}$ ($\text{E} = \text{S}$ (**54**), Se (**55**)) forms. On reaction of E_4^{2-} with elemental chalcogen and iron carbonyl, the larger cluster $[\text{Fe}_6(\text{CO})_{12}\text{E}_6]^{2-}$ (**56**) is isolated. The zero-valent complexes of Ni and Pd, ML_4 ($\text{M} = \text{Ni}$, Pd ; $\text{L} = \text{Co}$, PPh_3) are oxidized to formal M(II) state on reaction with **55**, and mixed-metal complexes are formed that consist of two $[\text{Fe}_2(\text{CO})_6\text{E}_2]^{2-}$ groups chelating to a divalent heterometal ion in a square-planar coordination environment. The structure of $[\text{Ph}_4\text{P}]_2[\{\text{Fe}_2(\text{CO})_6(\mu_3\text{-S})_2\}\text{Ni}]$ (**57**) (Fig. 15) has been established by X-ray methods.⁵⁰

The anionic tetrahedral clusters $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})]^{2-}$ ($\text{E} = \text{S}$ (**52**), Se (**53**), Te (**48**)) can be obtained from the thermolytic reaction of K_2E with $[\text{Fe}(\text{CO})_5]$ in DMF. Although a lone pair of electrons is present on E, investigations of the reactivity of electrophiles and oxidants toward the lone pair of electrons on the apical Te atom in **48** suggest strongly that the apical Te atom is unreactive toward electrophiles and that reaction occurs at metal centers (Scheme 3).⁵⁰

That the nature of the polytelluride solution plays an important role is also borne out by studies of the chromium–telluride system. If the polytellurides are prepared *in situ* by the reaction of elemental potassium with elemental tellurium in DMF, the products are considerably cleaner and can be obtained in higher yields than when the polytelluride source is a premade potassium salt, such as K_2Te_2 or K_2Te_3 . It has been suggested that equilibria are occurring in the reaction flask. Pure Te_2^{2-} and Te_3^{2-} can be prepared in pure form in liquid ammonia, but there is no evidence for the formation of higher tellurides in the presence of alkali metal counter-



SCHEME 3.

ions.^{51,52} Higher tellurides, Te_4^{2-} and Te_5^{2-} , are the dominant species in polar organic solvents, particularly in the presence of large organic counterions.^{53–55}

The reactions of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with the soluble polytellurides Te_x^{2-} ($x = 1–4$) have been investigated using a threefold excess of the metal carbonyls. For instance, reaction of a threefold excess of Group 6 metal carbonyl with a solution containing a reduced telluride anion of nominal composition Te_2^{2-} yields $[\text{M}_4(\text{CO})_{18}(\mu_3\text{-Te})_2]^{2-}$ ($\text{M} = \text{Cr}$ (**58**), Mo (**59**), W (**60**)), which has been isolated as its PPh_4^+ salt. The structures of chromium and tungsten species have been determined, and the molybdenum analog has been found to be isomorphous with the other two. Each structure contains a metal–metal bonded dimer of two metal–tetracarbonyl fragments. The dimer is bridged by two tellurides, generating a planar four-membered ring. Each tellurium ligand is also attached to a metal–pentacarbonyl group, one above and one below the ring. The metal–metal

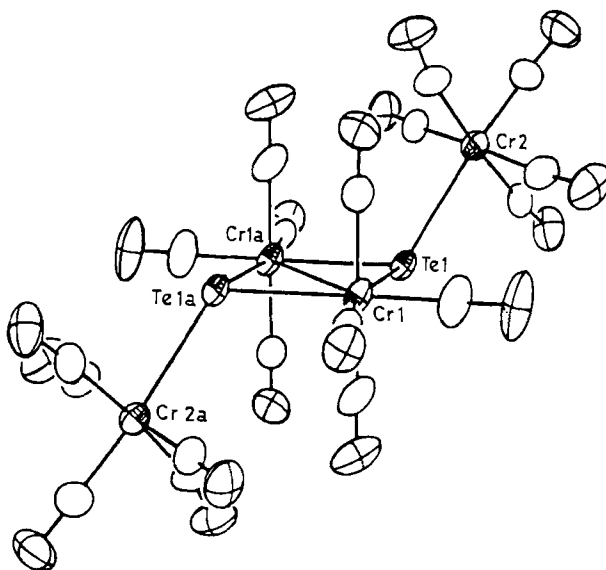


FIG. 16. Molecular structure of $[\text{Cr}_4(\text{CO})_{18}(\mu_3\text{-Te})_2]^{2-}$ (**58**). [Reprinted with permission from Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1992**, *31*, 2056. Copyright 1992 American Chemical Society.]

bond distance in **60** (3.115(1) Å) is somewhat longer than typical S- or Se-bridged tungsten–tungsten distances, which are in the vicinity of 2.90 Å,⁵⁶ and has been attributed to the larger size of tellurium. The existence of a metal–metal bond is supported by magnetic susceptibility data that reveal the molecules to be diamagnetic. The Cr–Cr distance in **58** (Fig. 16) is also somewhat long at 3.052(2) Å, which is again attributable to the presence of large bridging tellurium ligands.

The use of a more reduced telluride solution, namely, that of nominal composition Te^{2-} with $\text{Cr}(\text{CO})_6$, yields an unusual cluster, $[\{\text{Cr}(\text{CO})_5\}_4\text{Te}_2]^{2-}$ (**61**) (Fig. 17), as the sole product, isolable as its $(\text{PPh}_4)^+$ salt. The tungsten and molybdenum analogs of this compound are not formed. The structure of the **61** dianion consists of a Te_2^{2-} chain that is attached to four $\text{Cr}(\text{CO})_5$ groups, two on each tellurium atom.

In contrast to the preceding two reactions, when a less reduced form of polytelluride is used, such as salts of nominal composition K_2Te_3 , K_2Te_4 , Te_3^{2-} , Te_4^{2-} prepared *in situ* or crystalline $[\text{Ph}_4\text{P}]_2[\text{Te}_4]$, the cluster $[\{\text{Cr}(\text{CO})_5\}_4\text{Te}_3][\text{Ph}_4\text{P}]_2$ (**62**) is obtained readily. The tungsten and molybdenum analogs of this cluster are not formed. The structure of the **62** (Fig. 18) dianion consists of a Te_3^{2-} chain and two chromium–pentacarbonyl groups bonded to each end of the tritelluride chain.⁵⁷

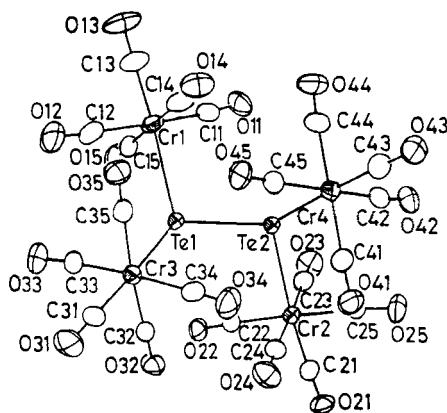


FIG. 17. Molecular structure of $[\{Cr(CO)_5\}_4Te_2]^{2-}$ (**61**). [Reprinted with permission from Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1992**, *31*, 2056. Copyright 1992 American Chemical Society.]

The reaction of $W(CO)_6$ with $[Ph_4P]_2[Te_4]$ at $100^\circ C$ in DMF solvent generates the complex $[\{W(CO)_3\}_6(Te_2)_4]^{2-}$ (**63**) (Fig. 19). Its structure consists of a central ditelluride group that is side-bonded to three W_2Te_2 units, creating a three-membered paddle wheel with the Te_2 group as its axis. Each of the paddles is joined by another Te_2 group. Three carbonyl groups are terminally bonded to each W atom. The central $Te-Te$ group has a $Te-Te$ distance of $2.855(2)$ Å, which can be considered within bonding distance (in elemental Te, the $Te-Te$ distance is 2.84 Å).⁵⁸ The outer

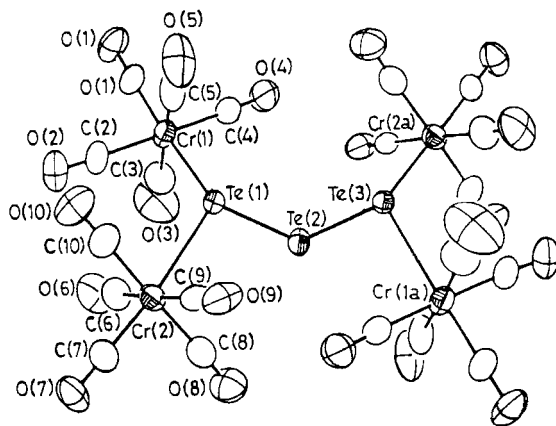


FIG. 18. Molecular structure of $[\{Cr(CO)_5\}_4Te_3][PPh_4]_2$ (**62**). [Reprinted with permission from Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1992**, *31*, 2056. Copyright 1992 American Chemical Society.]

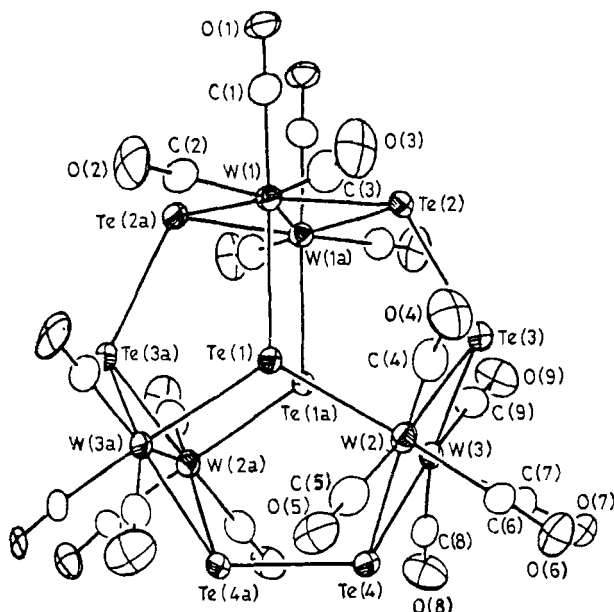


FIG. 19. Molecular structure of $[(W(CO)_3Te_2)_4]^{2-}$ (**63**). [Reprinted with permission from Roof, L. C.; Pennington, W. T.; Kolis, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 8172. Copyright 1990 American Chemical Society.]

shell of this cluster is similar to the outer shell of the hcp fragment in $[Rh_{13}(CO)_{24}]^{5-}$ (**64**),⁵⁹ the main difference being that instead of an interstitial metal atom, this molecule contains a ditelluride group holding it together.³²

C. Synthesis of Fe/Mo/S Clusters by Reduction of $Fe_2S_2(CO)_6$

The neutral complex $[Fe_2(CO)_6S_2]$ (**65**) is known to undergo reduction to form the disulfide-bridged dimeric compound $[Fe_4S_4(CO)_{12}]^{2-}$ (**66**),⁶⁰ which on further reduction yields $[Fe_2(CO)_6S_2]^{2-}$ (**67**).^{61,62} The nucleophilic character of the bridging sulfides in the fully reduced dianion **67** is demonstrated by its reaction with a variety of metal halides to yield metal clusters in which the butterfly unit of **67** acts as a bidentate ligand coordinated via the bridging sulfides.^{63–66} With alkyl halides, **67** reacts to form S-alkylated products.^{60,63}

Reaction of **66** with $FeBr_2$ forms the cluster $[Fe_5S_4(CO)_{12}]^{2-}$ (**68**). One-electron oxidation of **68** by ferrocenium ion or $[Fe(phen)_3]^{3+}$ results in quantitative conversion to the monoanion analog $[Fe_5S_4(CO)_{12}]^-$ (**69**). The

monoanion can also be prepared by reaction of 1 eq FeBr_2 with a solution containing 1 eq **67** and 0.5 eq **66**, or by reaction of FeBr_3 with 2 eq **67**. Structures of **68** (Fig. 20) and **69** (Fig. 21) have been determined by X-ray methods to be identical.⁶⁷

Cluster **68** reacts with oxygen to produce $[\text{Fe}_6\text{S}_6(\text{CO})_{12}]^{2-}$ (**70**) (Fig. 22).⁵⁰

Reaction of **67** with MoCl_5 produces the Fe–S clusters **68** and **70**, as well as the Fe–Mo–S clusters $[\text{Fe}_5\text{MoOS}_6(\text{CO})_{12}]^{2-}$ (**71**) and $[\text{Fe}_4\text{Mo}_2\text{O}_4(\text{CO})_{12}]^{2-}$ (**72**).⁶⁸ Reaction of $[\text{Mo}(\text{CO})_4\text{I}_3]^-$ with 2–3 eq **67** produces $[\text{Fe}_6\text{MoS}_6(\text{CO})_{16}]^{2-}$ (**73**) (Fig. 23) and $[\text{Fe}_4\text{MoS}_3(\text{CO})_{14}]^{2-}$ (**74**). The structure of **74** has been determined in the form of its triethyl phosphine derivative, $[\text{Fe}_4\text{MoS}_3(\text{CO})_{13}(\text{PET}_3)]^{2-}$ (**75**) (Fig. 24).

On reaction of $[\text{Mo}(\text{CO})_4\text{I}_3]^-$ with 1 eq **67**, the $[\text{Fe}_2\text{Mo}_2\text{S}_2(\text{CO})_{12}]^{2-}$ cluster (**76**) (Fig. 25) is obtained.⁶⁹

D. Influence of Stoichiometry on Formation of Fe/Se Clusters

When an aqueous solution of K_2SeO_3 is treated with 1 eq $\text{Fe}(\text{CO})_5/\text{KOH}$ in methanol, an anionic carbonyl species that decomposes in solution to $\text{Fe}_2\text{Se}_2(\text{CO})_6$ (**77**) is observed to be formed. **77** can be isolated as the $[\text{PhCH}_2\text{NMe}_3]^+$ salt and has been characterized as $[\text{PhCH}_2\text{NMe}_3][\text{Se}_6\text{Fe}_6(\text{CO})_{12}]$ (**78**) (Fig. 26).

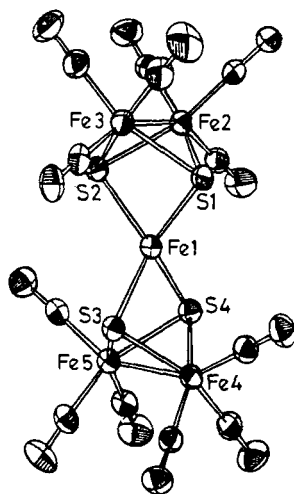


FIG. 20. Molecular structure of $[\text{Fe}_5(\text{CO})_{12}\text{S}_4]^{2-}$ (**68**). [Reprinted with permission from Barber, D. E.; Sabat, M.; Sinn, E.; Averill, B. A. *Organometallics* **1995**, *14*, 3229. Copyright 1995 American Chemical Society.]

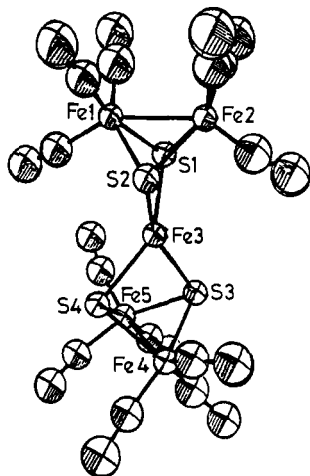


FIG. 21. Molecular structure of $[\text{Fe}_5(\text{CO})_{12}\text{S}_4]^{2-}$ (**69**). [Reprinted with permission from Barber, D. E.; Sabat, M.; Sinn, E.; Averill, B. A. *Organometallics* **1995**, *14*, 3229. Copyright 1995 American Chemical Society.]

Its core geometry consists of two $\text{Fe}_2\text{Se}_2(\text{CO})_6$ units, each attached to one Fe atom of a central $[\text{Fe}_2\text{Se}_2]^{2-}$ anion. It is proposed to be an intermediate for the formation of **77** from the reaction of SeO_3^{2-} with basic $\text{Fe}(\text{CO})_5$ solution, followed by acidification (Scheme 4).

Indeed, on acidification, **78** affords **77**. When a 1 : 3 ratio of K_2SeO_3 and $\text{Fe}(\text{CO})_5/\text{KOH}$ is used, formation of $[\text{SeFe}_3(\text{CO})_9]^{2-}$ (**79**) is observed, which on acidification affords $\text{Fe}_3\text{Se}_2(\text{CO})_9$ (**80**). Careful manipulation of reactant stoichiometry has enabled the observation of several anionic species. This has been elegantly done by employing solid K_2SeO_3 to react with 1 eq $\text{Fe}(\text{CO})_5/\text{KOH}$ in methanol solvent. The low solubility of K_2SeO_3 in methanol allows for a gradual increase of SeO_3^{2-} concentration, resulting in

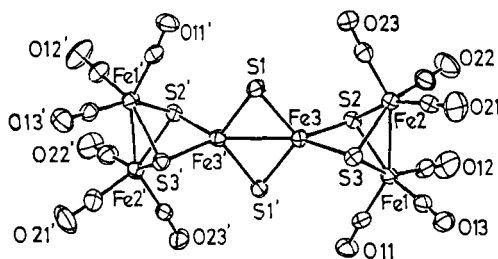


FIG. 22. Molecular structure of $[\text{Fe}_6(\text{CO})_{12}\text{S}_6]^{2-}$ (**70**). [Reprinted with permission from Holliday, R. L.; Roof, I. C.; Hargus, B.; Smith, D. M.; Wood, P. T.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1995**, *34*, 4392. Copyright 1995 American Chemical Society.]

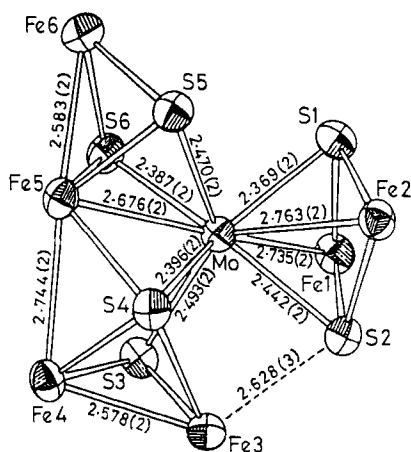


FIG. 23. Molecular structure of $[\text{Fe}_6\text{MoS}_6(\text{CO})_{16}]^{2-}$ (**73**). [Reprinted with permission from Eldredge, P. A.; Bose, K. S.; Barber, D. E.; Bryan, R. F.; Sinn, E.; Rheingold, A. L.; Averill, B. A. *Inorg. Chem.* **1991**, 30, 2365. Copyright 1991 American Chemical Society.]

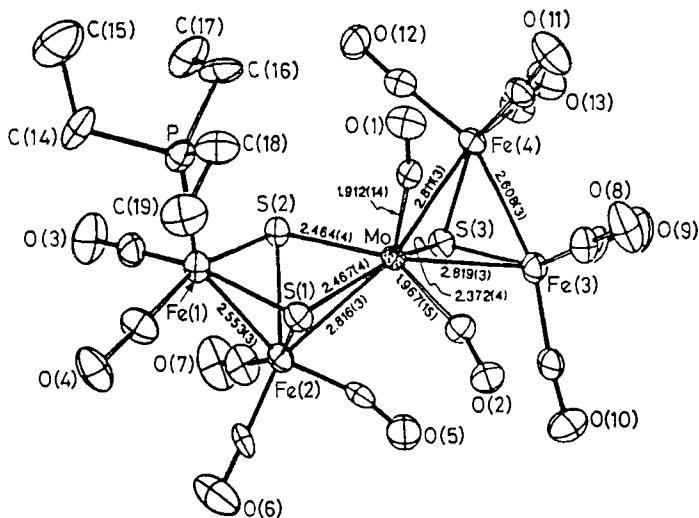


FIG. 24. Molecular structure of $[\text{Fe}_4\text{MoS}_3(\text{CO})_{13}(\text{PET}_3)]^{2-}$ (**75**). [Reprinted with permission from Eldredge, P. A.; Bose, K. S.; Barber, D. E.; Bryan, R. F.; Sinn, E.; Rheingold, A. L.; Averill, B. A. *Inorg. Chem.* **1991**, 30, 2365. Copyright 1991 American Chemical Society.]

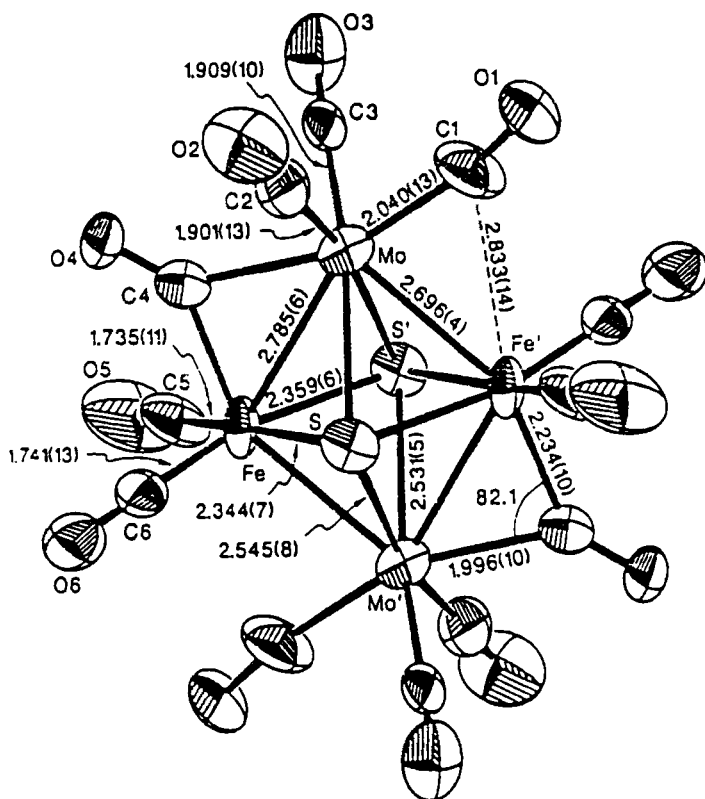


FIG. 25. Molecular structure of $[\text{Fe}_2\text{Mo}_2\text{S}_2(\text{CO})_{12}]^{2-}$ (76). [Reprinted with permission from Eldredge, P. A.; Bose, K. S.; Barber, D. E.; Bryan, R. F.; Sinn, E.; Rheingold, A. L.; Averill, B. A. *Inorg. Chem.* **1991**, 30, 2365. Copyright 1991 American Chemical Society.]

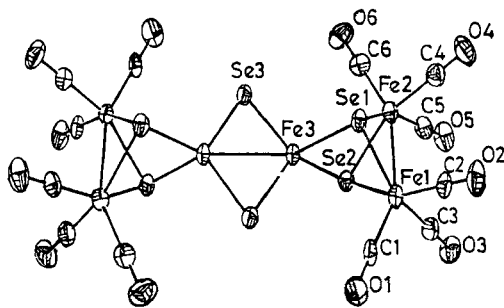
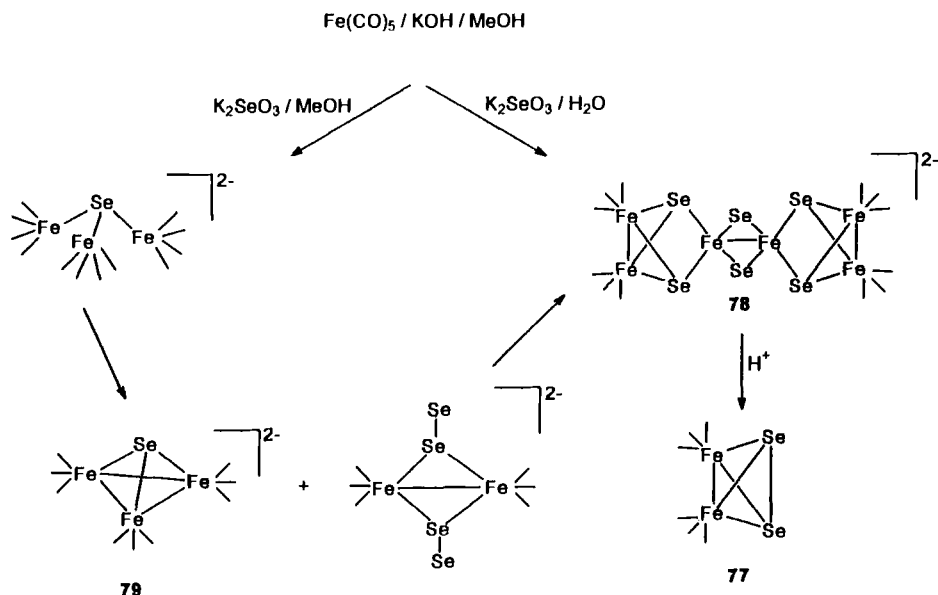


FIG. 26. Molecular structure of $[\text{PhCH}_2\text{NMe}_3][\text{Se}_6\text{Fe}_6(\text{CO})_{12}]$ (78). [Reprinted with permission from Shieh, M.; Shieh, M.-H.; Tsai, Y.-C.; Ueng, C.-H. *Inorg. Chem.* **1995**, 34, 5088. Copyright 1995 American Chemical Society.]



SCHEME 4.

formation of several anionic species, each at a particular concentration of SeO_3^{2-} .⁷⁰

The hydrides $[\text{H}_{2-n}\text{Fe}_3\text{S}(\text{CO})_9]^{n-}$ ($n = 0$ (**81**), 1 (**82**)) can be obtained by a self-assembling reaction of $[\text{HFe}(\text{CO})_4]^-$ and S^{2-} ions on acidification^{71,72} or the reduction under a CO atmosphere of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ with *t*-BuLi.⁷³ Reaction of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ with piperidine–sulfur adduct affords

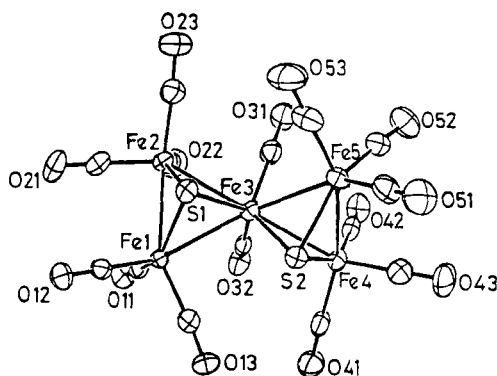


FIG. 27. Molecular structure of $[\text{Fe}_5(\mu_3\text{-S})_2(\text{CO})_{14}]^{2-}$ (**85**). [Reprinted with permission from Calderoni, F.; Demartin, F.; Iapalucci, M. C.; Laschi, F.; Longoni, G.; Zanello, P. *Inorg. Chem.* **1996**, 35, 898. Copyright 1996 American Chemical Society.]

$[\text{Fe}_3\text{S}(\text{CO})_9]^{2-}$ (**83**) in 60–70% yield, with SCL_2 , in 70% yield.⁷⁴ On further addition of sulfur–piperidine adduct or of SCL_2 , **83** is converted to $[\text{Fe}_6(\mu_3\text{-S})_4(\mu_2\text{-S})_2(\text{CO})_{12}]^{2-}$ (**84**), which can also be obtained from $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ by treatment with sulfur–piperidine. The orange-red **83** is converted to $[\text{Fe}_5(\mu_3\text{-S})_2(\text{CO})_{14}]^{2-}$ (**85**) on treatment with AgBF_4 . The **85** (Fig. 27) dianion can also be obtained directly from either $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ or $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ by reaction with SCL_2 .

IV

NEUTRAL CLUSTERS

A. Tetranuclear Clusters and Substituted Derivatives

The vacuum pyrolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with PhSeSePh at 185°C affords the tetraruthenium cluster $[\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-Se})_2]$ (**86**) (Fig. 28) as the only isolable product.⁷⁵ By contrast, the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with PhSeSePh under mild conditions produces $[\text{Os}_3(\text{SePh})_2(\text{CO})_{10}]$ (**87**). Apparently, only the Se–Se bond of PhSeSePh is cleaved in this process.^{76,77} In the reaction with the kinetically more labile $[\text{Ru}_3(\text{CO})_{12}]$ (compared with $[\text{Os}_3(\text{CO})_{12}]$) and with the use of more-forcing pyrolysis conditions, the Se–Se and Se–C bonds rupture and fragmentation of the carbonyl cluster takes place. Isolation of **86** as the major component suggests that this may

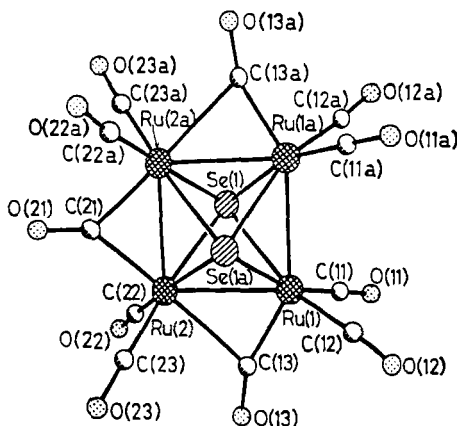


FIG. 28. Molecular structure of $[\text{Ru}_4(\mu_4\text{-Se})_2(\text{CO})_{11}]$ (**86**). [Reprinted with kind permission from Johnson, B. F. G.; Layer, T. M.; Lewis, J.; Martin, A.; Raithby, P. R. Synthesis and characterisation of novel selenium-containing clusters: crystal structures of $[\text{Ru}_4(\mu_4\text{-Se})_2(\text{CO})_8(\mu\text{-CO})_3]$ and $[\text{Ru}_3(\mu_3\text{-Se})_2(\text{CO})_7(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)]$. *J. Organomet. Chem.* **1992**, 429, C41. Copyright 1992 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

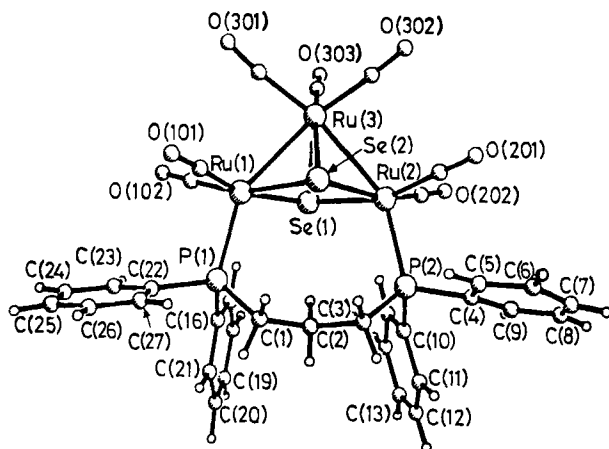


FIG. 29. Molecular structure of $[\text{Ru}_3(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\mu_3\text{-Se})_2(\text{CO})_7]$ (**89**). [Reprinted with permission from Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc., Dalton Trans.* **1982**, 1881. Copyright 1982 Royal Society of Chemistry.]

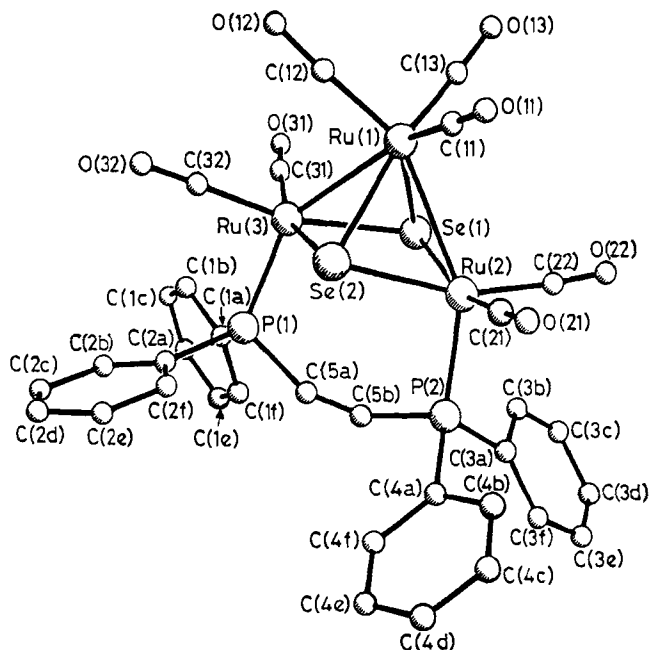


FIG. 30. Molecular structure of $[\text{Ru}_3(\text{dppa})(\mu_3\text{-Se})_2(\text{CO})_7]$ (**90**). [Reprinted with permission from Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc., Dalton Trans.* **1982**, 1881. Copyright 1982 Royal Society of Chemistry.]

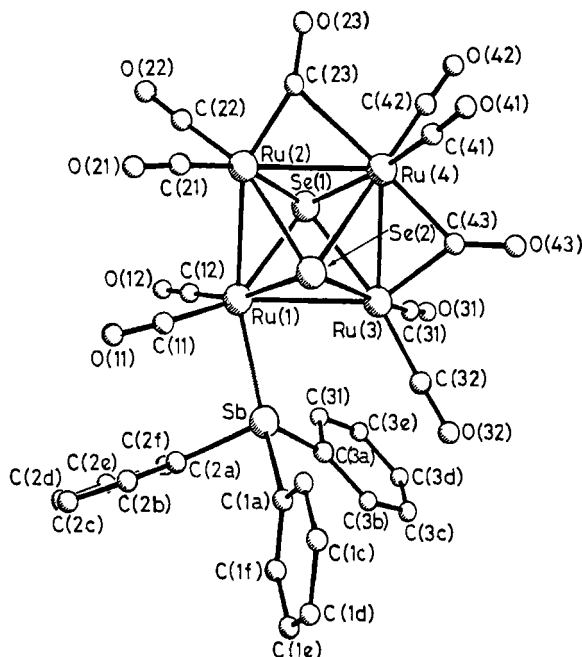


FIG. 31. Molecular structure of $[\text{Ru}_4(\text{SbPh}_3)(\mu_4\text{-Se})_2(\text{CO})_{10}]$ (**96**). [Reprinted with permission from Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc., Dalton Trans.* **1982**, 1881. Copyright 1982 Royal Society of Chemistry.]

be the thermodynamically favored product. The cluster **86** has also been prepared by thermolysis reaction of $[\text{Ru}_3(\text{CO})_{12}]$ and **80** or by the room-temperature reaction of $[\text{Ru}_3\text{Se}_2(\text{CO})_9]$ (**88**) with $[\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)]$.⁷⁸

At room temperature, **86** reacts with a wide range of ligands to form two types of products, those arising from substitution of one or more carbonyl groups with the Ru_4Se_2 cluster framework remaining intact, and those in which the Ru_4Se_2 framework is degraded to a Ru_3Se_2 framework. It reacts with 1,3-bis(diphenylphosphinopropane) or bis(diphenylphosphino)acetylene (dppa) to form the triruthenium clusters $[\text{Ru}_3(\text{CO})_7\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}(\mu_3\text{-Se})_2]$ (**89**) (Fig. 29) or $[\text{Ru}_3(\text{CO})_7(\text{dppa})(\mu_3\text{-Se})_2]$ (**90**) (Fig. 30).⁷⁹ With triphenylphosphine, it forms $[\text{Ru}_4\text{Se}_2(\text{CO})_{10}(\text{PPh}_3)]$ (**91**), $[\text{Ru}_4\text{Se}_2(\text{CO})_9(\text{PPh}_3)_2]$ (**92**), $[\text{Ru}_3\text{Se}_2(\text{CO})_8(\text{PPh}_3)]$ (**93**), $[\text{Ru}_3\text{Se}_2(\text{CO})_7(\text{PPh}_3)_2]$ (**94**), and $[\text{Ru}_3\text{Se}_2(\text{CO})_6(\text{PPh}_3)_3]$ (**95**). With SbPh_3 , it reacts at room temperature without undergoing any fragmentation to form the monosubstituted product $[\text{Ru}_4(\mu_4\text{-Se})_2(\text{CO})_{10}(\text{SbPh}_3)]$ (**96**) (Fig. 31), which is isomorphous and isostructural with the tellurium-capped analog, $[\text{Ru}_4(\mu_4\text{-Te})_2(\text{CO})_{10}(\text{PPh}_3)]$ (**97**).⁸⁰

86 reacts with CO under a pressure of 70 atm to form **88**. The action of CO effectively decaps the substrate carbonyl **86**, by a mechanism that might be similar to the one noted in the preparation of the pentanuclear ruthenium carbido cluster $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ (**98**) by the direct carbonylation of $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ (**99**).⁸¹

The Te-bridged cluster $[\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-Te})_2]$ (**100**) (Fig. 32) has been prepared by the thermolysis reaction of $[\text{Fe}_3\text{Te}_2(\text{CO})_9]$ (**101**) and $[\text{Ru}_3(\text{CO})_{12}]$.⁸⁰

The clusters **56** and **100** have identical heavy-atom frameworks and similar disposition of the carbonyl ligands. The core consists of a trapezoidal arrangement of four Ru atoms that is capped on each face by a quadruply bridging chalcogen atom. The shortest metal–metal bond contains a bridging carbonyl ligand. The longest edge of the trapezoid is opposite to the CO-bridged edge, and the two remaining edges are associated with semi-bridging carbonyl ligands. The same structures are also observed for the related S-bridged clusters, $[\text{Fe}_4(\text{CO})_{11}(\mu_4\text{-S})_2]$ (**102**), which have been obtained from the photolysis of $[\text{Fe}_3\text{S}_2(\text{CO})_9]$ (**103**) and $[\text{Fe}(\text{CO})_5]$ ⁸² and

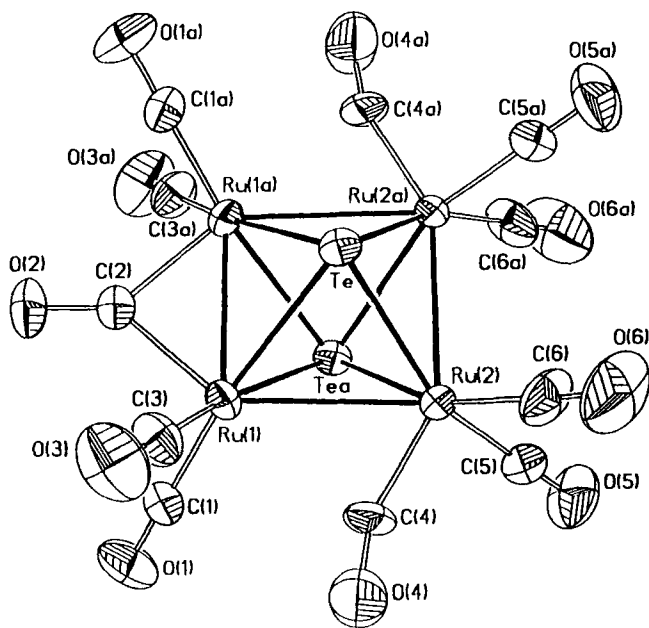


FIG. 32. Molecular structure of $[\text{Ru}_4(\mu_4\text{-Te})_2(\text{CO})_{11}]$ (**100**). [Reprinted with permission from Mathur, P.; Thimmappa, B. H. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, 29, 4658. Copyright 1990 American Chemical Society.]

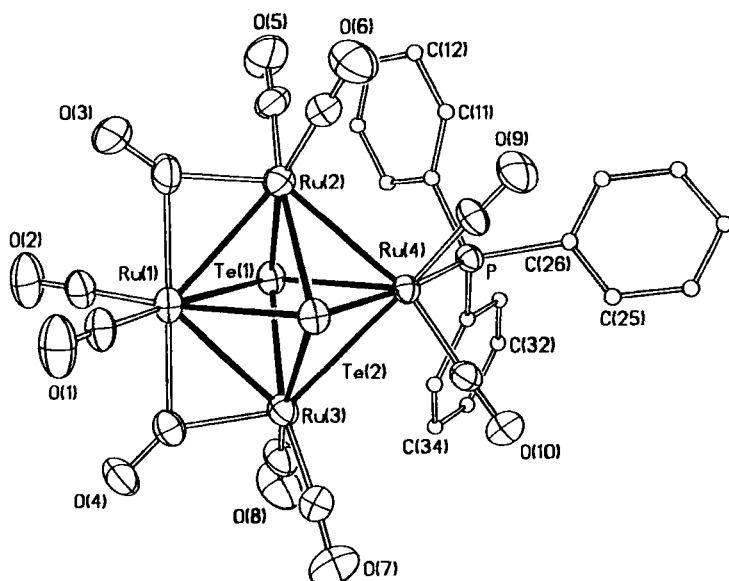


FIG. 33. Molecular structure of $[\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)(\mu_4\text{-Te})_2]$ (**106**). [Reprinted with permission from Mathur, P.; Thimmappa, B. H. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, 29, 4658. Copyright 1990 American Chemical Society.]

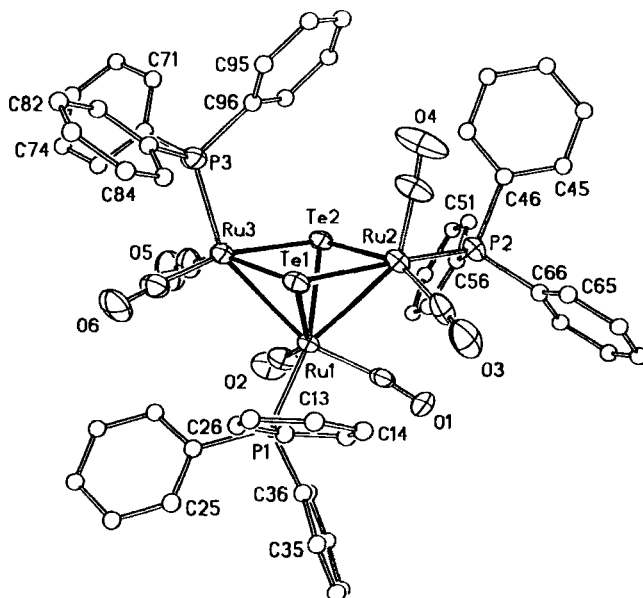


FIG. 34. Molecular structure of $[\text{Ru}_3(\text{CO})_6(\text{PPh}_3)_3(\mu_3\text{-Te})_2]$ (**107**). [Reprinted with permission from Mathur, P.; Thimmappa, B. H. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, 29, 4658. Copyright 1990 American Chemical Society.]

$[\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-S})_2]$ (**104**), whose structure has been determined in the form of the bis(phosphine)-substituted derivative, $[\text{Ru}_4\text{S}_2(\text{CO})_9(\text{PMe}_2\text{Ph})_2]$ (**105**).⁸³ With phosphine ligands, **100** also gives both tetra- and triruthenium clusters. When a solution of **100** is stirred at room temperature with triphenylphosphine, $[\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)(\mu_4\text{-Te})_2]$ (**106**) (Fig. 33) and the trisphosphine derivative, $[\text{Ru}_3(\text{CO})_6(\text{PPh}_3)_3(\mu_3\text{-Te})_2]$ (**107**) (Fig. 34), are formed. With bis(diphenylphosphino)methane, the cluster framework is retained, and two carbonyl groups are substituted to form $[\text{Ru}_4(\text{CO})_9(\text{dppm})(\mu_4\text{-Te})_2]$ (**108**).

B. Formation of Clusters Under Facile Conditions

The mixed-metal cluster $[\text{Fe}_2\text{Ru}_2(\text{CO})_{11}(\mu_4\text{-Te})_2]$ (**109**) (Fig. 35) has been obtained in a stepwise manner under facile reaction conditions. Room-

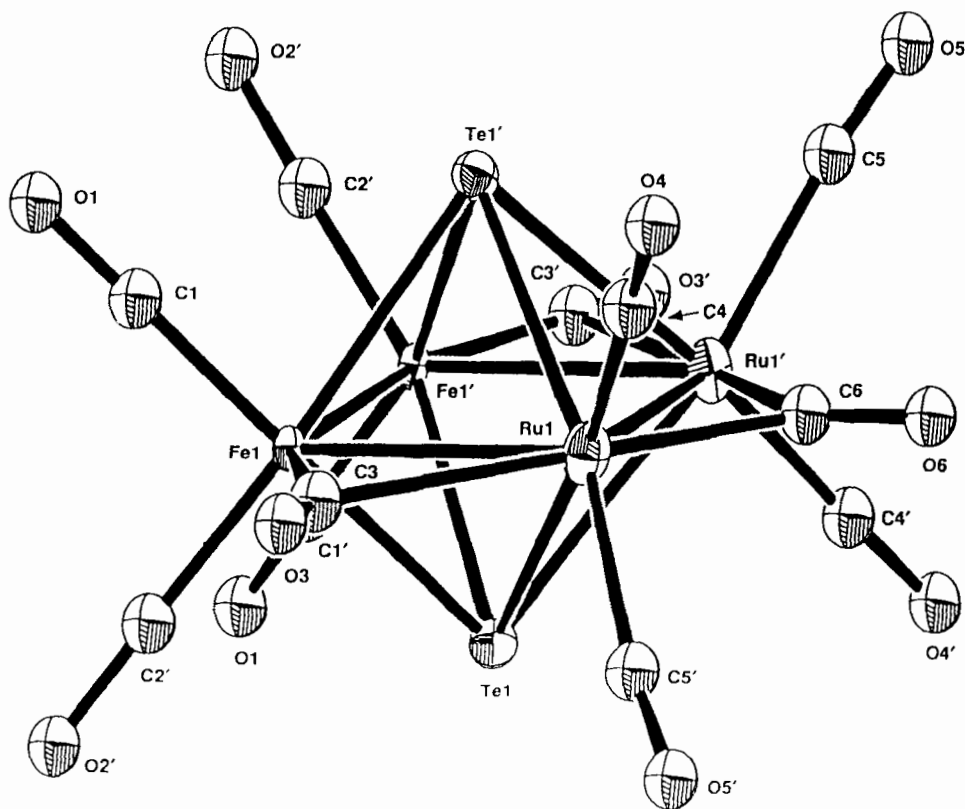
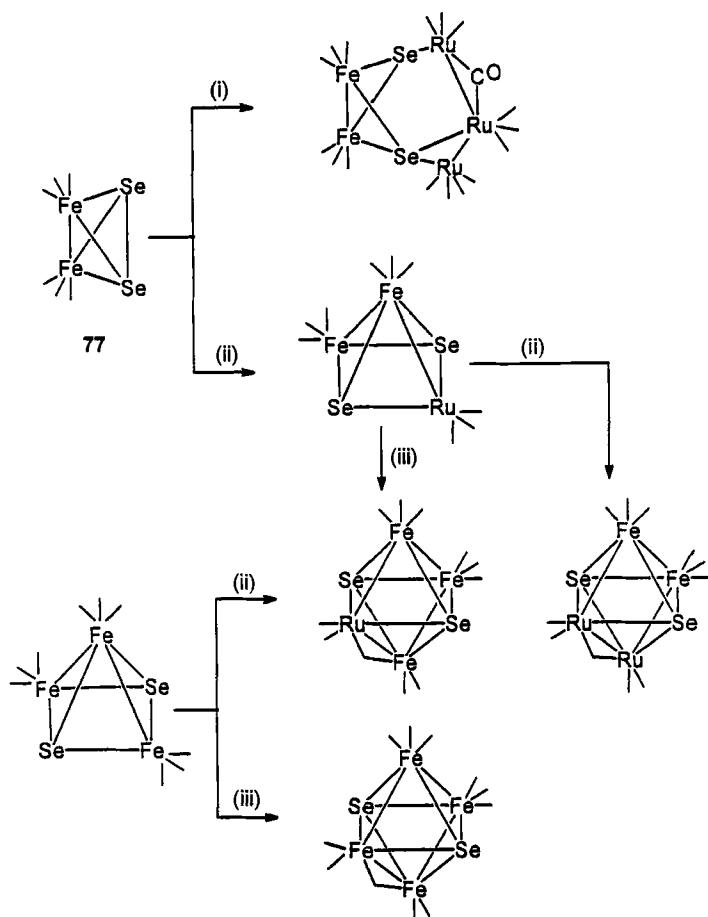


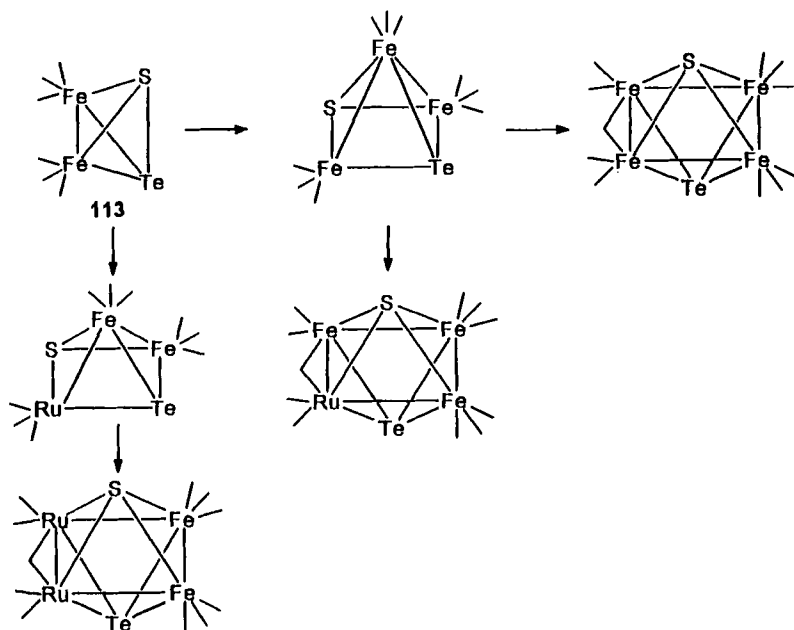
FIG. 35. Molecular structure of $[\text{Fe}_2\text{Ru}_2(\mu_4\text{-Te})_2(\text{CO})_{11}]$ (**109**). [Reprinted with permission from Mathur, P.; Mavunkal, I. J.; Rugmini, V.; Mahon, M. F. *Inorg. Chem.* **1990**, 29, 4838. Copyright 1990 American Chemical Society.]

temperature reaction of $[\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)]$ (**110**) with freshly prepared $[\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)]$ forms $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-Te})_2]$ (**111**), which can react further with $[\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)]$ to form **109**.⁸⁴ This strategy is useful for obtaining mixed-metal clusters of desired compositions, as shown in Scheme 5.⁸⁵

Availability of the mixed-chalcogenide complexes $[\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')] (E, E' = \text{SSe (112), STe (113), SeTe (114)})$ provides easy access to mixed-metal, mixed-chalcogenide clusters with the use of room-temperature conditions (Scheme 6).⁸⁶



SCHEME 5.



SCHEME 6.

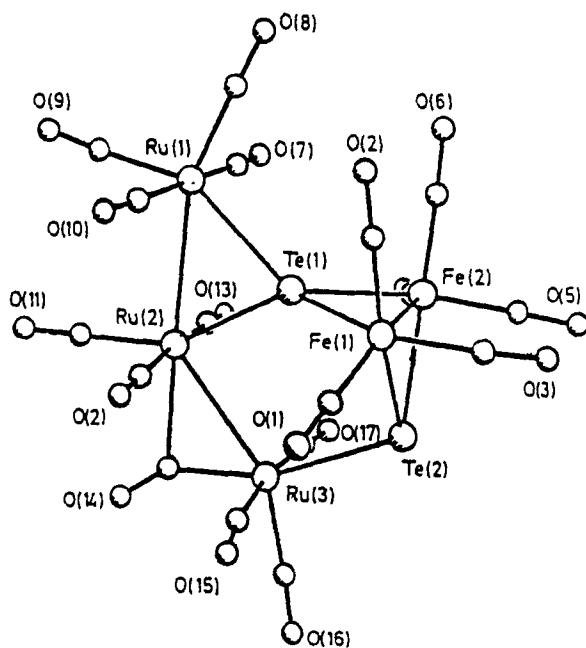


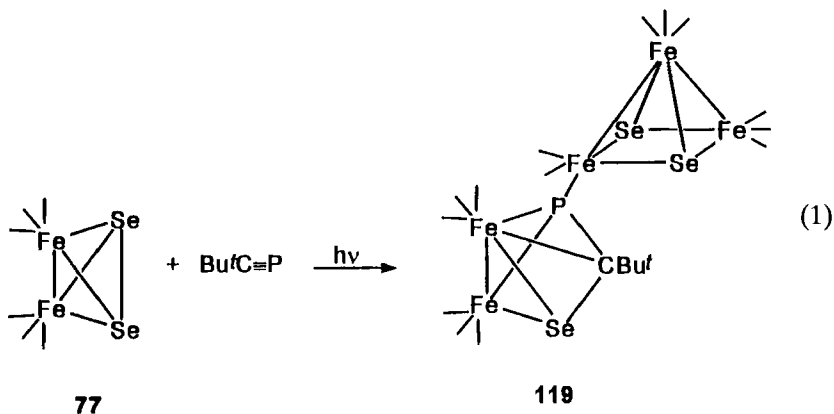
FIG. 36. Molecular structure of $\{[\text{Fe}_2(\text{CO})_6](\mu_4\text{-Te})(\mu_3\text{-Te})\{\text{Ru}_3(\text{CO})_{11}\}\}$ (**115**). [Reprinted with permission from Mathur, P.; Mavunkal, L. J.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 382. Copyright 1989 Royal Society of Chemistry.]

Addition of polynuclear groups across the Te-Te bond of **110** occurs readily. For instance, at room temperature, $[\text{Ru}_3(\text{CO})_{12}]$ or $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ react with **110** to form $[\{\text{Fe}_2(\text{CO})_6\}(\mu_4\text{-Te})(\mu_3\text{-Te})\{\text{Ru}_3(\text{CO})_{11}\}]$ (**115**) (Fig. 36)⁸⁷ or $[\{\text{Fe}_2(\text{CO})_6\}(\mu_4\text{-Te})(\mu_3\text{-Te})\{\text{Os}_3(\text{CO})_{11}\}]$ (**116**),⁸⁸ respectively.

When the bis-acetonitrile complexes $[\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2]$ or $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ are used, atom-transfer reactions are observed and $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-Te})_2]$ (**117**) or $[\text{Os}_3(\text{CO})_9(\mu_3\text{-Te})_2]$ (**118**), respectively, are formed. On photolysis or thermolysis, both **115** and **116** yield the respective trinuclear compounds, **117** or **118**.⁸⁸

C. Alkyne and Dialkyne Derivatives

On photolysis with ultraviolet light of a hexane solution containing **77** and $t\text{-BuC}\equiv\text{P}$, an unusual cluster, $[\{\text{Fe}_3\text{Se}_2(\text{CO})_8\}(\mu\text{-PC-}t\text{-Bu})\{\text{Fe}_2\text{Se}(\text{CO})_6\}]$ (**119**) [Eq. (1)] (Fig. 37), is obtained.⁸⁹



Its structure can be described as consisting of both a Fe_3Se_2 square-pyramidal core and a Fe_2Se triangular unit linked by a $t\text{-BuCP}$ group that is η^1 -bonded to one of the basal Fe atoms of the Fe_3Se_2 unit and to both Fe atoms of the Fe_2Se unit. The C atom of the bridging phosphaaalkyne is bonded to one Fe atom and the Se atom of the Fe_2Se unit. When a hexane solution of **77** is photolyzed in the absence of phosphaaalkyne, formation of insoluble black material is observed, and after extraction, small amounts of **77** and **80** are obtained. The presence of the phosphaaalkyne in the reaction medium thus serves to bridge these two species, leading to the formation of **119** with an overall loss of one Se atom.

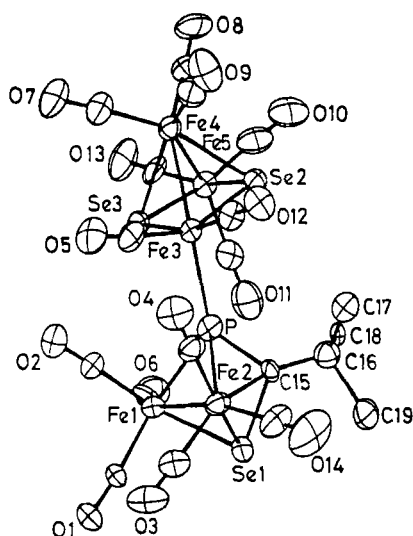


FIG. 37. Molecular structure of $[(\text{Fe}_3\text{Se}_2(\text{CO})_8)(\mu\text{-PC-}i\text{-Bu})\{\text{Fe}_2\text{Se}(\text{CO})_6\}]$ (**119**). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Hitchcock, P. B.; Nixon, J. F. *Organometallics* **1995**, *14*, 3101. Copyright 1995 American Chemical Society.]

Abstraction of a bridging Se ligand during the course of a reaction is observed in the formation of the unusual cluster $[\{(\mu\text{-BuSe})\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-Se})]$ (**120**) (Fig. 38) from the reaction of a monoanion, derived from **77** and *n*-BuLi, with 1,3-dibromopropane.⁹⁰ Its structure consists of two identical $[(\mu\text{-BuSe})\text{Fe}_2(\text{CO})_6]$ moieties joined to a unique selenium atom. In the cluster core, the unique selenium is situated at the center of a distorted tetrahedron with four iron atoms at its apices. The geometry of the $\mu_4\text{-Se}$ ligand here is similar to that of $\mu_4\text{-S}$ found in $[\{(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]$ (**121**),^{91,92} $[\{(\mu\text{-SMe})\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]$ (**122**),⁹³ $\mu_4\text{-Sn}$ in $[\{\text{Fe}_2(\text{CO})_8(\mu_2\text{-Sn}(\text{CH}_3)_2)_2(\mu_4\text{-Sn})\}]$ (**123**),⁹⁴ $\mu_4\text{-As}$ in $[\text{Co}_4(\eta^5\text{-C}_5\text{H}_5)_4(\text{CO})_4(\mu_4\text{-As})]^+$ (**124**),⁹⁵ $\mu_4\text{-CO}$ in $[\text{Me}_3\text{NCH}_2\text{Ph}][\text{Fe}_4(\text{CO})_{12}\text{H}(\mu_4\text{-CO})]$ (**125**),⁹⁶ and $\mu_4\text{-Sb}$ in $[\{\text{Fe}_2(\text{CO})_8(\mu_4\text{-Sb})\}_2\text{Fe}_2(\text{CO})_6]$ (**126**).⁹⁷

Room-temperature stirring of phenylacetylene and **77** forms the adduct $[(\text{CO})_6\text{Fe}_2\{(\mu\text{-SeC}(\text{Ph})\text{C}(\text{H})\text{Se})\}]$ (**127**) (Fig. 39), as well as $[\{(\text{CO})_6\text{Fe}_2(\mu\text{-Se})_2\}_2\text{C}(\text{Ph})\text{C}(\text{H})]$ (**128**).⁹⁸

The structure of **127** consists of a Fe_2Se_2 butterfly core with the phenylacetylene molecule attached to the wing-tip Se atoms of the butterfly, and that of **128** consists of two Fe_2Se_2 butterfly units that are linked to each other through a bridging $\text{PhC}-\text{CH}$ group (Fig. 40). The acetylenic C–C bond distances in the two compounds are 1.331(7) and 1.48(1) Å, respectively, corresponding to C–C double and single bond orders.

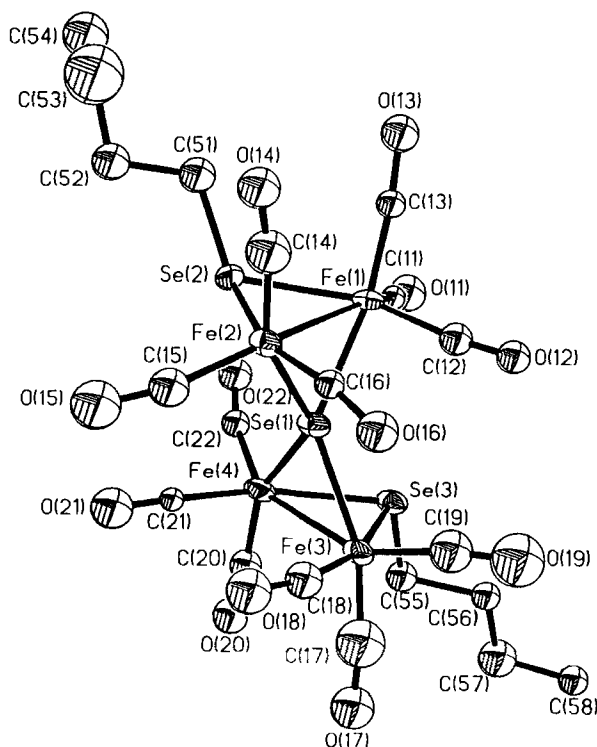


FIG. 38. Molecular structure of $\{[(\mu\text{-BuSe})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-Se})\}$ (**120**). [Reprinted with permission from Mathur, P.; Trivedi, R.; Satyanarayana, C. V. V. *Organometallics* **1996**, *15*, 1062. Copyright 1996 American Chemical Society.]

The double butterfly compound **128** undergoes a pairwise C–Se bond cleavage on reaction with $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ at room temperature, and three compounds are isolated from the reaction mixture (Scheme 7).⁹⁹ With bis(diphenylphosphino)ethane it undergoes CO substitution and forms $\{[(\text{CO})_5\text{Fe}_2(\mu\text{-Se})_2]\text{C}(\text{Ph})\text{C}(\text{H})(\mu\text{-dppe})\}$ (**129**) (Fig. 41). The double-butterfly core is retained and one dppe group is attached to one Fe atom of each Fe_2Se_2 unit.

The compound $\{[(\text{CO})_6\text{Fe}_2\text{Pt}(\text{PPh}_3)_2\{\mu\text{-SeC}(\text{Ph})\text{C}(\text{H})\}]\}$ (**130**) (Fig. 42) has also been made by the room-temperature reaction of **127** with $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$, and its structure has been determined crystallographically.¹⁰⁰

The acetylenic C–C bond distance of 1.423(15) Å in **130** is longer than in **127**, consistent with the transformation of the acetylene ligand from a formal 2-electron donor to a 4-electron donor.

Different isomers are possible from the reaction of phenylacetylene

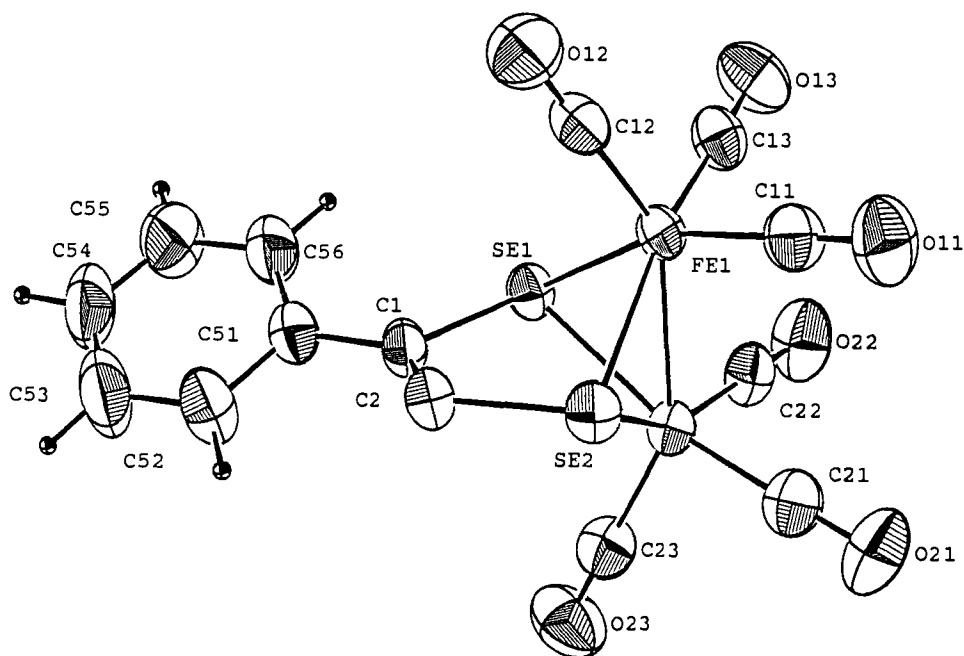


FIG. 39. Molecular structure of $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(Ph)C(H)Se}\}]$ (**127**). [Reprinted with permission from Mathur, P.; Hossain, M. M. *Organometallics* **1993**, *12*, 2398. Copyright 1993 American Chemical Society.]

with the mixed-chalcogenide compounds $[\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')]$ (**112**, **113**, and **114**) (Scheme 8).¹⁰¹ For instance, the room-temperature reaction of **112** with phenylacetylene results in the formation of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC(H)=C(Ph)Te}\}]$ (**131**) (Fig. 43) and $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC(Ph)=C(H)Te}\}]$ (**132**). The room-temperature reaction of **111** with phenylacetylene also forms two isomeric products, $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC(H)=C(Ph)Te}\}]$ (**133**) (Fig. 44) and $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC(Ph)=C(H)Te}\}]$ (**134**). From the reaction of **110** with phenylacetylene, only one isomer is observed, $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC(Ph)=C(H)Se}\}]$ (**135**) (Fig. 45). The use of ^{77}Se and ^{125}Te NMR spectroscopy has been found to be useful in identifying the different isomers because of the large differences between long- and short-range Se–H and Te–H couplings.

When acetylene gas is bubbled through a methanol solution of **112**, **113**, or **114** in the presence of sodium acetate, the acetylene adducts $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC(H)=C(H)Se}\}]$ (**136**), $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC(H)=C(H)Te}\}]$ (**137**), or $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC(H)=C(H)Te}\}]$ (**138**), respectively, are formed in good yields.¹⁰² The Se compounds $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC(H)=C(H)Se}\}]$ (**139**) and $[\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-C(H)-C(H)}\}]$ (**140**) have been isolated from the room-

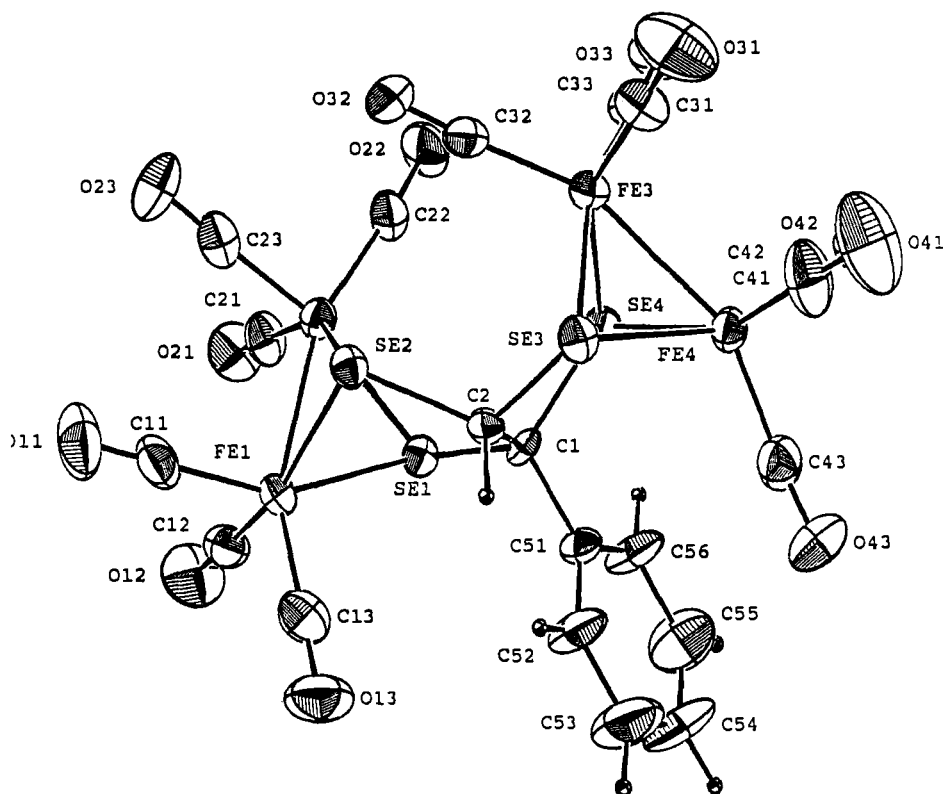
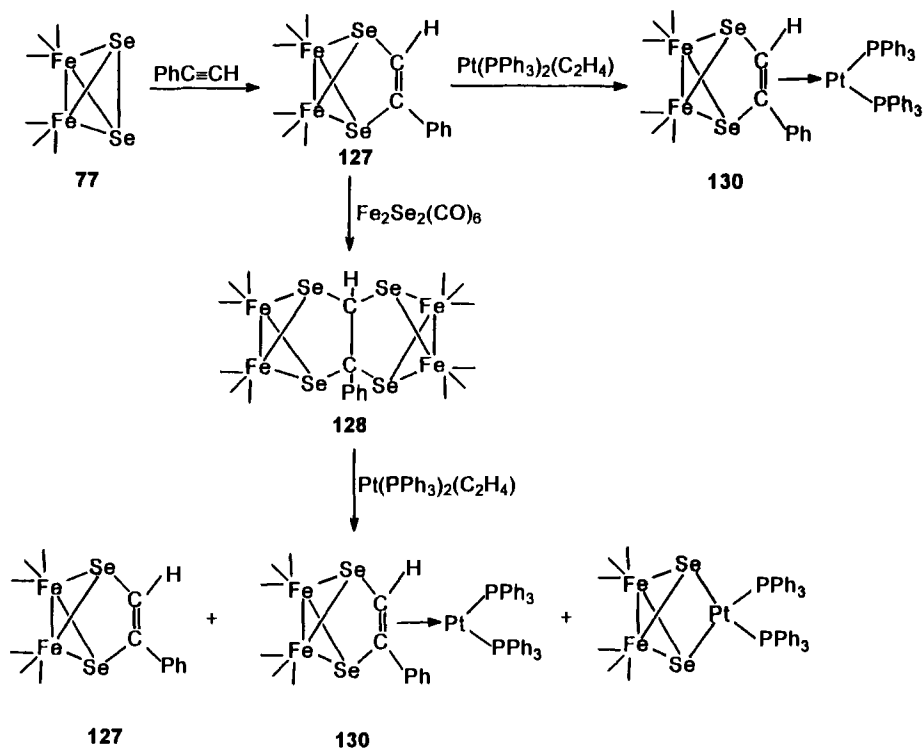


FIG. 40. Molecular structure of $[(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)_2\text{C}(\text{Ph})\text{-C}(\text{H})]$ (**128**). [Reprinted with permission from Mathur, P.; Hossain, M. M. *Organometallics* **1993**, *12*, 2398. Copyright 1993 American Chemical Society.]

temperature reaction **77** with acetylene in methanol-solvent-containing sodium acetate. Although their structures have not been determined by crystallographic methods, their identification is unambiguous on the basis of comparison of their spectroscopic features with those of the related phenylacetylene adducts, **127** and **128**. The S_2 analog, $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC}(\text{H})=\text{C}(\text{H})\text{S}\}]$ (**141**), has been obtained by a different method, by reacting $\text{HC}\equiv\text{CMgBr}$ with **65**, followed by protonation with $\text{CF}_3\text{CO}_2\text{H}$.¹⁰³ It is suggested that the higher reactivity of the mixed-chalcogenide compounds towards the acetylenes, substituted or unsubstituted, is possibly due to partial decomposition of $[\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')]$ in solution, with liberation of $\text{Fe}(\text{CO})_x$ fragments that may influence the reactivity of acetylenes toward these systems. The involvement of $\text{Fe}(\text{CO})_x$ fragments in these reactions is probably only one of several factors contributing to the difference in reactivity observed. The nature of the R group in $\text{RC}\equiv\text{CH}$ is important

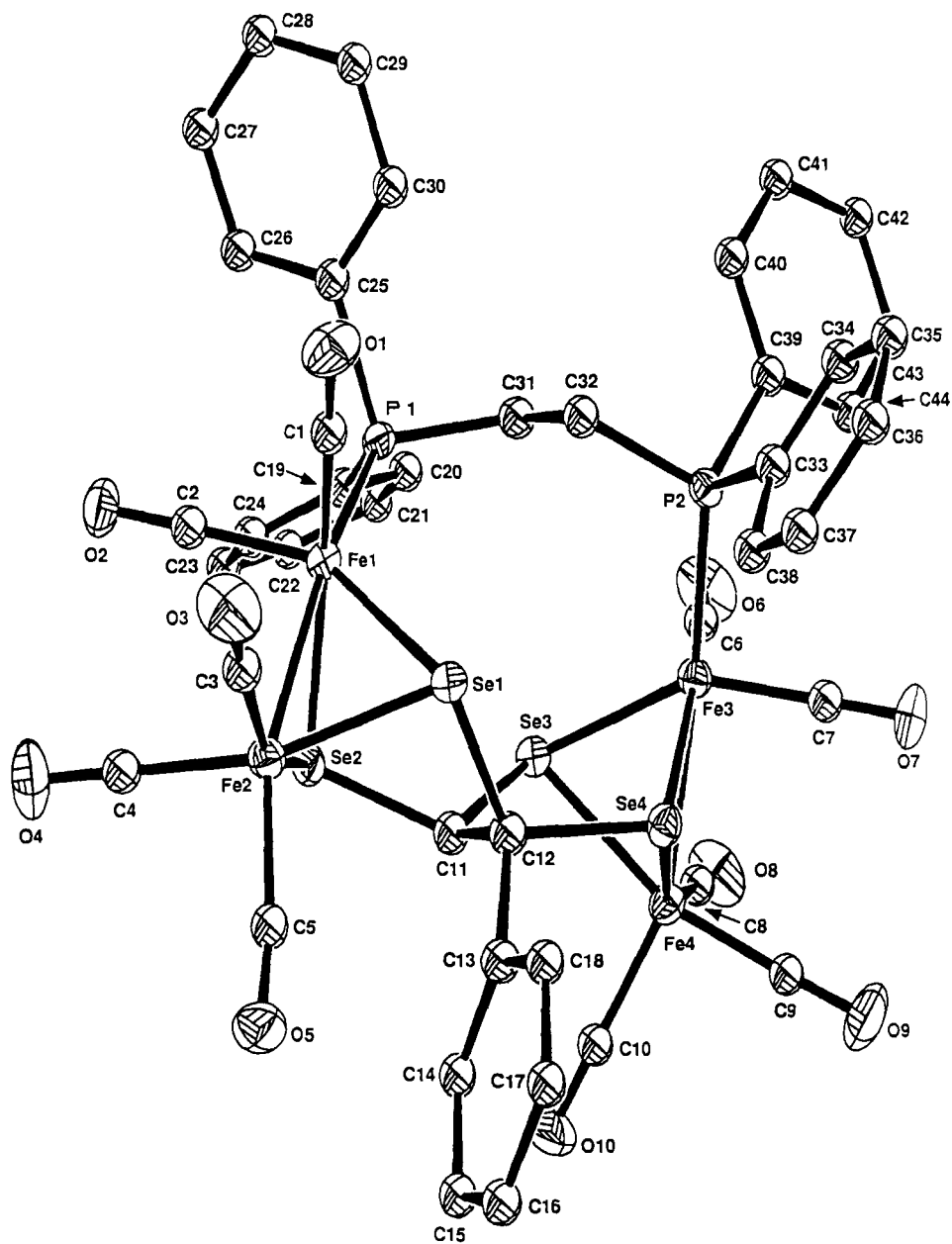


SCHEME 7.

in controlling the addition of the acetylenic triple bond across the $\text{E}-\text{E}'$ bond. For instance, whereas acetylene readily adds to **110**, phenylacetylene is inert towards such addition. Under thermolytic conditions, **101** reacts with phenylacetylene to form $[\text{Fe}_2(\text{CO})_6\{\mu\text{-TeC}(\text{H})=\text{C}(\text{Ph})\text{Te}\}]$ (**142**).¹⁰⁴ It is thought that the $\text{Fe}(\text{CO})_3$ fragments formed as a result of fragmentation of **101** under reaction conditions effect the addition of phenylacetylene to **110**.¹⁰⁵

The addition of diacetylenes to the compounds $[\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)]$ occurs readily and the type of product formed depends on the nature of the substituent on the diacetylene.¹⁰⁶ For instance, **77** reacts with $\text{HC}\equiv\text{CC}\equiv\text{R}$ ($\text{R} = \text{SiMe}_3$ or $(n\text{-Bu})_3\text{Sn}$) at room temperature in methanol containing sodium acetate to yield $[\{\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)\}_2(\mu\text{-S-trans-C}_4\text{H}_2)]$ (**143**) (Fig. 46), in which a 1,3-butadiene ligand is coordinated to the Fe_2Se_2 core in a *trans* conformation as determined by X-ray diffraction studies.

By contrast, the substituted diacetylenes add to **77** such that the substituted acetylenic bond remains uncoordinated. At room temperature, $\text{HC}\equiv\text{CC}\equiv\text{R}$ ($\text{R} = \text{Me}$ or $n\text{-Bu}$) add to the Se atoms of **77** to form



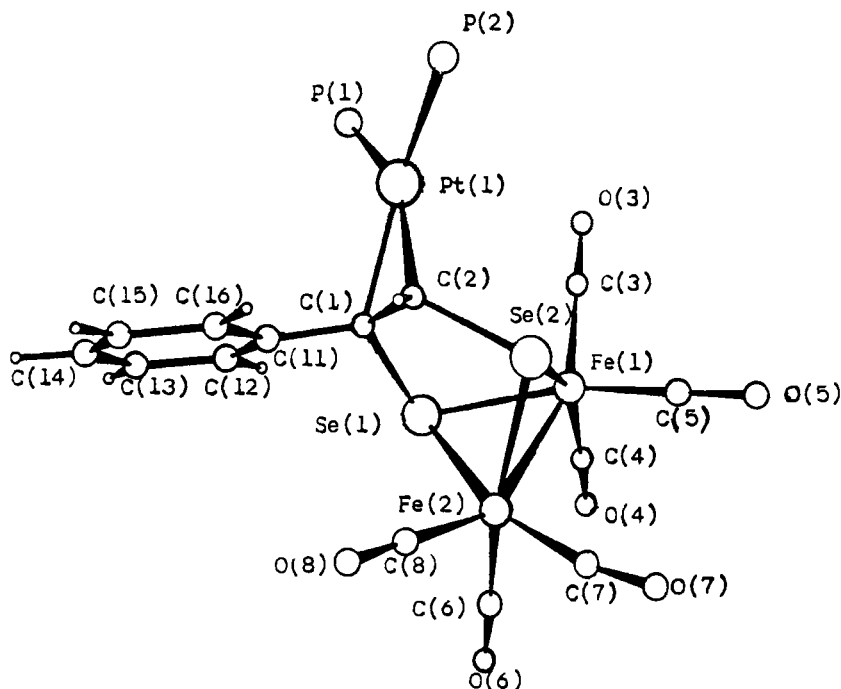
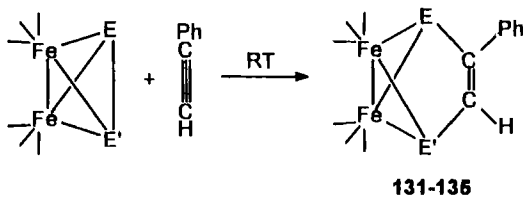


FIG. 42. Molecular structure of $[(\text{CO})_6\text{Fe}_2\text{Pt}(\text{PPh}_3)_2\{\mu\text{-SeC}(\text{Ph})\text{C}(\text{H})\}]$ (**130**). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Das, K.; Sinha, U. C. *J. Chem. Soc., Chem. Commun.* **1993**, 46. Copyright 1993 Royal Society of Chemistry.]

$[\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}]$ ($\text{R} = \text{Me}$ (**144**) (Fig. 47), $n\text{-Bu}$ (**145**)). Also formed in these reactions are the compounds $[\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-HC}-\text{C}(\text{C}\equiv\text{CR})\}]$ ($\text{R} = \text{Me}$ (**146**) (Fig. 48), $n\text{-Bu}$ (**147**)).

The uncoordinated triple bonds in compounds $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{H})=\text{C}(\text{C}\equiv\text{CR})\text{Se}\}]$ have been used for the addition of various metal–carbonyl groups to form clusters of the form $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-C}(\text{H})=\text{C}(\text{CCR})\}\text{M}]$ ($\text{M} = \text{Os}_3(\text{CO})_{10}$, $\text{R} = \text{Me}$ (**148**) (Fig. 49), $n\text{-Bu}$ (**149**); $\text{M} = \text{Ru}_3(\text{CO})_{10}$, $\text{R} = \text{Me}$ (**150**) (Fig. 50), $n\text{-Bu}$ (**151**); $\text{M} = \text{Cp}_2\text{Mo}_2(\text{CO})_4$, $\text{R} = \text{Me}$ (**152**), $n\text{-Bu}$ (**153**) (Fig. 51); $\text{M} = \text{Co}_2(\text{CO})_6$, $\text{R} = \text{Me}$ (**154**), $n\text{-Bu}$ (**155**)).^{107,108}

FIG. 41. Molecular structure of $[\{(\text{CO})_5\text{Fe}_2(\mu\text{-Se})_2\text{C}(\text{Ph})\text{C}(\text{H})(\mu\text{-dppe})\}]$ (**129**). [Reprinted with kind permission from Mathur, P.; Hossain, M. M.; Mahon, M. F. Carbon-selenium bond cleavage in the double butterfly complex $[\{(\text{CO})_6\text{Fe}_2(\mu\text{-Se})_2\}_2\text{C}(\text{Ph})\text{-C}(\text{H})\}]$. *J. Organomet. Chem.* **1994**, 471, 185. Copyright 1994 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]



E	E'
Te	Se
Se	Te
S	Se
Te	S
S	Te

SCHEME 8.

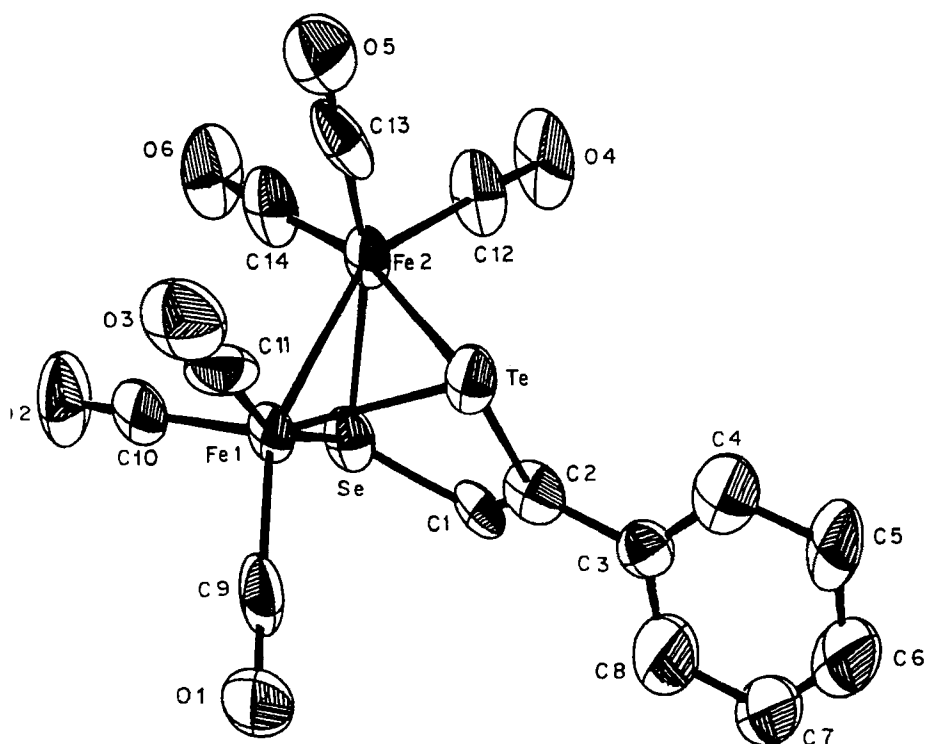


FIG. 43. Molecular structure of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC(Ph)=C(H)Te}\}]$ (**131**). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Umbarkar, S. B.; Satyanarayana, C. V. V.; Tavale, S. S.; Puranik, V. G. *Organometallics* **1995**, *14*, 959. Copyright 1995 American Chemical Society.]

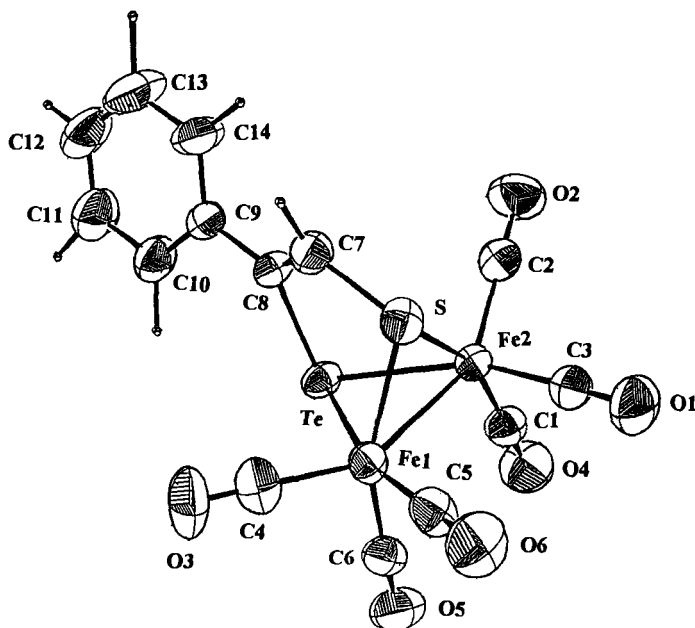


FIG. 44. Molecular structure of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC(Ph)=C(H)Te}\}]$ (**133**). [Reprinted with permission from Mathur, P.; Dash, A. K.; Hossain, M. M.; Umbarkar, S. B.; Satyanarayana, C. V. V.; Chen, Y.-S.; Holt, E. M.; Rao, S. N.; Soriano, M. *Organometallics* **1996**, *15*, 1356. Copyright 1996 American Chemical Society.]

The mixed-chalcogenide compound **113** also adds $\text{MeC}\equiv\text{CC}\equiv\text{CH}$ across its S–Te bond to form $[(\text{CO})_6\text{Fe}_2\text{STe}\{\mu\text{-C(H)=C(C}\equiv\text{CMe)}\}]$ (**156**) (Fig. 52).¹⁰⁹ Of the four possible isomers, only one is observed, that which has the $\text{C(C}\equiv\text{CMe)}$ group farthest away from the larger chalcogen atom.

This is, in principle, in agreement with extended Hückel molecular-orbital calculations. The calculated binding energy and difference between the energies of the LUMO and HOMO for the four possible isomers indicate the experimentally isolated structure to be the most stable one, although the extended Hückel calculation does not show a substantial relative stability (Table I).

D. Reaction of $\text{Fe}_2(\text{CO})_9\text{E}_2$ and $\text{Fe}_3(\text{CO})_9\text{E}_2$ with Diazoalkanes

The reaction of $[\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')] (E = E', E, E' = \text{S (65), Se (77), Te (110)})$ and of mixed-chalcogenide compounds (**112–114**) with diazoethane forms two types of compounds (Scheme 9): one in which the C(H)CH_3 group formally inserts into the chalcogen–chalcogen bond $(\text{CO})_6\text{Fe}_2$

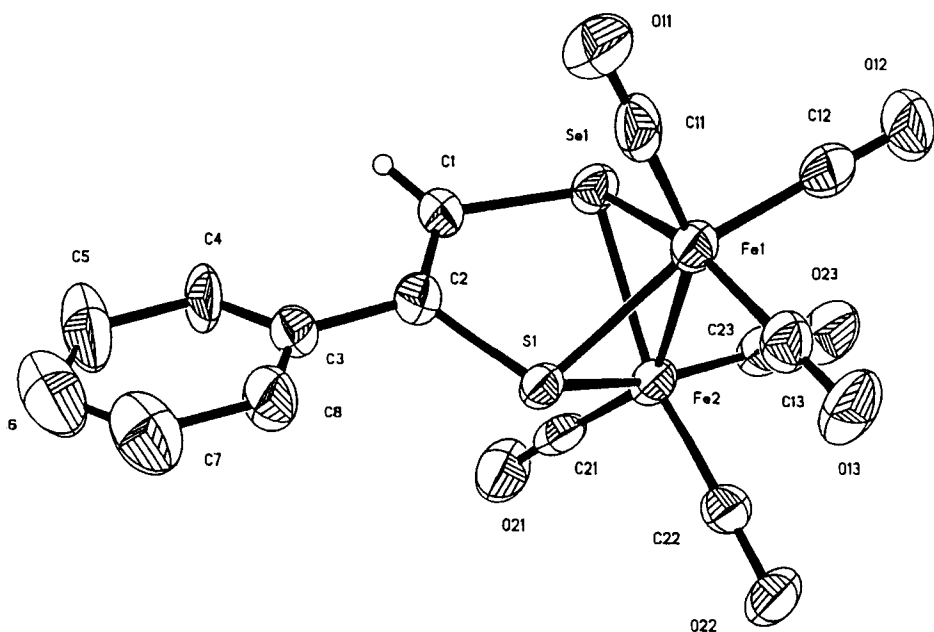


FIG. 45. Molecular structure of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC(Ph)=C(H)Se}\}]$ (**135**). [Reprinted with permission from Mathur, P.; Dash, A. K.; Hossain, M. M.; Umbarkar, S. B.; Satyanarayana, C. V. V.; Chen, Y.-S.; Holt, E. M.; Rao, S. N.; Soriano, M. *Organometallics* **1996**, *15*, 1356. Copyright 1996 American Chemical Society.]

$\{\mu\text{-EC(H)CH}_3\text{E}'\}$ (**157–160**), and another in which there is a formal Fe–Fe bond cleavage and the C(H)CH_3 group bridges the two Fe–chalcogen bonds to give a chairlike structure $(\text{CO})_6\text{Fe}_2\text{EE}'\{\mu\text{-C(H)CH}_3\}_2$ (**161–165**) (Fig. 53).¹¹⁰

There is a contrast in the reactivities for the different chalcogen combinations. In the case of **65** and **112**, the formation of only the chairlike structure is observed; insertion of the C(H)CH_3 group into the S–S or S–Se bond to form $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC(H)CH}_3\text{S})]$ or $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC(H)CH}_3\text{Se})]$ is not observed. Similarly, in the reaction of **110**, only $[\text{Fe}_2(\text{CO})_6(\mu\text{-TeC(H)CH}_3\text{Te})]$ (**160**) is formed; the chairlike compound is not observed. For all other chalcogen combinations, both types of structures are obtained. On the basis of relative yields of the two types of products obtained, it is seen that as the chalcogen atoms become larger and more electropositive, there is a greater preference for the chalcogen–chalcogen inserted compound to be formed at the expense of the chairlike compound.

Insertion of a methylene group into the Te–Te bond occurs readily on reaction of diazomethane with **110**.^{111,112} The structure of $[(\text{CO})_6\text{Fe}_2$

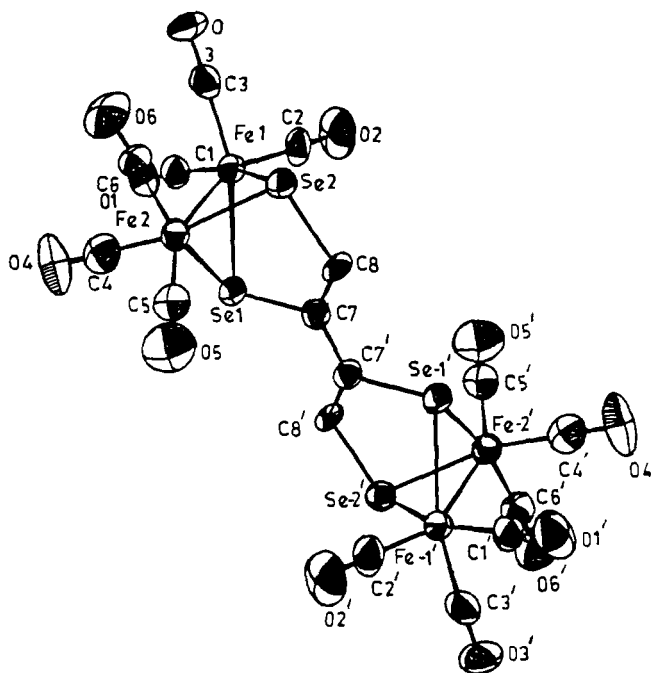


FIG. 46. Molecular structure of $[\text{Fe}_2(\text{CO})_6((\mu\text{-Se}_2)_2(\mu\text{-S-trans-C}_4\text{H}_2))]$ (**143**). [Reprinted with kind permission from Mathur, P.; Dash, A. K.; Hossain, M. M.; Satyanarayana, C. V. V.; Verghese, B. A chalcogen stabilised cluster containing a s-trans-1,3-diene. Synthesis and structural characterisation of $[\text{Fe}_2(\text{CO})_6((\mu\text{-Se}_2)_2(\mu\text{-s-trans-C}_4\text{H}_2))]$. *J. Organomet. Chem.* **1996**, 506, 307. Copyright 1996 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

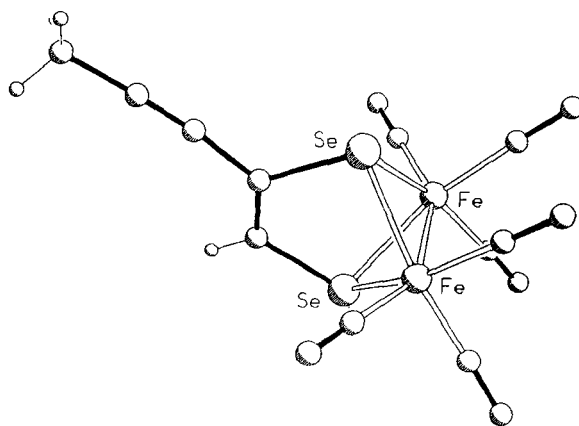


FIG. 47. Molecular structure of $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CMe})\}]$ (**144**). [Reprinted with kind permission from Mathur, P.; Hossain, M. M.; Rheingold, A. L. Diacetylene-bridged clusters: Synthesis and characterisation of $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}]$, $[\{\text{Fe}_2(\text{CO})_6(\text{Se}_2)_2\}\{\mu\text{-HC}-\text{C}(\text{C}\equiv\text{CR})\}]$ ($\text{R} = \text{Me}, \text{n-Bu}$) and $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC}-\text{C}(\text{CCMe})\}\text{Os}_3(\text{CO})_{10}]$. *J. Organomet. Chem.* **1996**, 507, 187. Copyright 1996 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

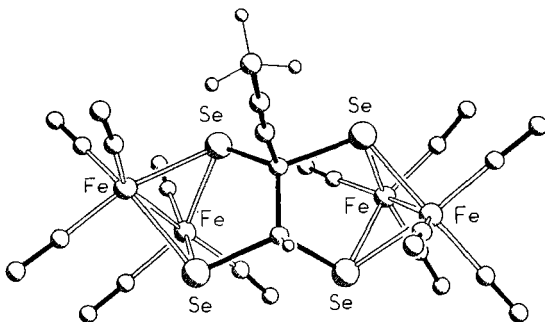


FIG. 48. Molecular structure of $[\{\text{Fe}_2(\text{CO})_6(\text{Se}_2)\}_2\{\mu\text{-HC-C}(\text{C}\equiv\text{CMe})\}]$ (**146**). [Reprinted with kind permission from Mathur, P.; Hossain, M. M.; Rheingold, A. L. Diacetylene-bridged clusters: Synthesis and characterisation of $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}]$, $[\{\text{Fe}_2(\text{CO})_6(\text{Se}_2)\}_2\{\mu\text{-HC-C}(\text{C}\equiv\text{CR})\}]$ ($\text{R} = \text{Me}, \text{n-Bu}$) and $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC-C}(\text{CCMe})\}\text{Os}_3(\text{CO})_{10}]$. *J. Organomet. Chem.* **1996**, 507, 187. Copyright 1996 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

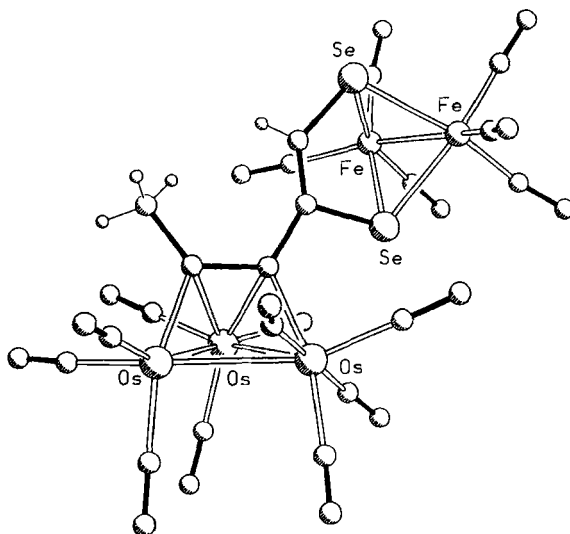


FIG. 49. Molecular structure of $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC-C}(\text{CCMe})\}\text{Os}_3(\text{CO})_{10}]$ (**148**). [Reprinted with kind permission from Mathur, P.; Hossain, M. M.; Rheingold, A. L. Diacetylene-bridged clusters: Synthesis and characterisation of $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}]$, $[\{\text{Fe}_2(\text{CO})_6(\text{Se}_2)\}_2\{\mu\text{-HC-C}(\text{C}\equiv\text{CR})\}]$ ($\text{R} = \text{Me}, \text{n-Bu}$) and $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC-C}(\text{CCMe})\}\text{Os}_3(\text{CO})_{10}]$. *J. Organomet. Chem.* **1996**, 507, 187. Copyright 1996 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

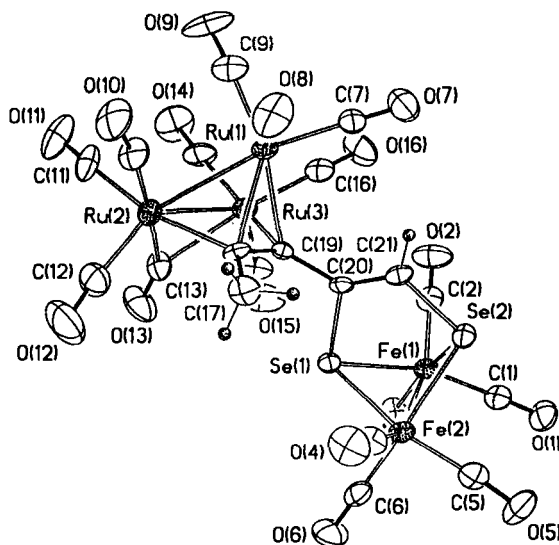


FIG. 50. Molecular structure of $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC-C}(\text{CCMe})\}\text{Ru}_3(\text{CO})_{10}]$ (**150**). [Reprinted with kind permission from Mathur, P.; Dash, A. K.; Hossain, M. M.; Satyanarayana, C. V. V.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. Diyne-bridged metal clusters: Synthesis and spectroscopic characterisation of $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC=C}(\text{CCR})\}]\text{M}$, ($\text{R} = \text{Me}$ and Bu^n ; $\text{M} = \text{Cp}_2\text{Mo}_2(\text{CO})_4$, $\text{Co}_2(\text{CO})_6$, $\text{Ru}_3(\text{CO})_{10}$ and $\text{Os}_3(\text{CO})_{10}$. Structural characterisation of $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC=C}(\text{CCBu}^n)\}]\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC=C}(\text{CCMe})\}]\text{Ru}_3(\text{CO})_{10}$. *J. Organomet. Chem.* in press. Copyright 1997 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

$(\mu\text{-TeCH}_2\text{Te})$] (**166**) (Fig. 54) has been established crystallographically. The same compound is also isolable when the trinuclear compound **101** is treated with diazomethane.

The reaction between **101** and diazomethane is sensitive to the stoichiometry of reagents. When a large excess of diazomethane is used, a double-butterfly compound is obtained, $[\{(\mu\text{-CH}_3\text{Te})\text{Fe}_2(\text{CO})_6\}_2\{\mu\text{-Te}(\text{CH}_2)\text{Te-}\mu\}]$ (**167**) (Fig. 55).¹¹³

A similar structure is observed for $[\{(\mu\text{-CH}_3\text{S})\text{Fe}_2(\text{CO})_6\}_2\{\mu\text{-S}(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{S-}\mu\}]$ (**168**), which can be obtained from the reaction of $[(\text{CO})_6\text{Fe}_2(\mu\text{-SCH}_3)(\mu\text{-S})]^-$ with $\text{BrMg}(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2)\text{MgBr}$.¹¹⁴

A nucleophilic metal anion has been used as a reducing agent to create Zintl ion directly. $[\text{PPN}]_2[\text{Fe}_2(\text{CO})_6(\text{Te}_2)_2]$ (**169**) has been synthesized by direct reaction of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ with elemental tellurium.¹¹⁵ Although not structurally characterized by X-ray methods, the formulation of **169** is supported by several pieces of experimental evidence. It can react with itself or with the Zintl ions present to produce mixed-metal species. It reacts with iodomethane to yield $[\text{Fe}_2(\text{CO})_6(\mu\text{-TeMe})_2]$ (**170**) (Fig. 56),

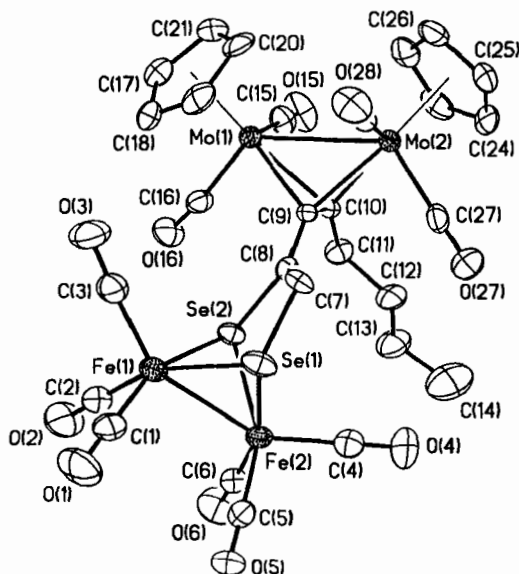


FIG. 51. Molecular structure of $[\text{Fe}_2(\text{CO})_6(\text{Se}_2)\{\mu\text{-HC-C}(\text{CC-}n\text{-Bu})\}\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ (**153**). [Reprinted with kind permission from Mathur, P.; Dash, A. K.; Hossain, M. M.; Satyanarayana, C. V. V.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. Diyne-bridged metal clusters: Synthesis and spectroscopic characterisation of $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC=C}(\text{CCR})\}]\text{M}$, ($\text{R} = \text{Me}$ and Bu^n ; $\text{M} = \text{Cp}_2\text{Mo}_2(\text{CO})_4$, $\text{Co}_2(\text{CO})_6$, $\text{Ru}_3(\text{CO})_{10}$ and $\text{Os}_3(\text{CO})_{10}$. Structural characterisation of $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC=C}(\text{CCBu}^n)\}]\text{Cp}_2\text{Mo}_2(\text{CO})_4$] and $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC=C}(\text{CCMe})\}]\text{Ru}_3(\text{CO})_{10}$]. *J. Organomet. Chem.* in press. Copyright 1997 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

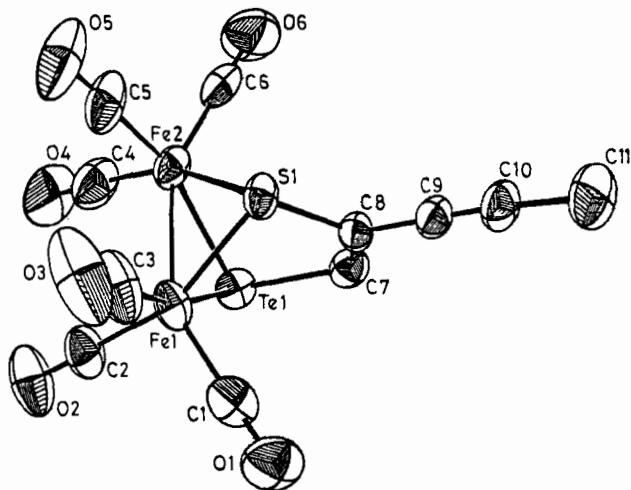


FIG. 52. Molecular structure of $[\text{Fe}_2(\text{CO})_6\text{STe}\{\mu\text{-HC=C}(\text{C}\equiv\text{CMe})\}]$ (**156**). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Datta, S. N.; Kondru, R. K.; Bhadbhade, M. M. *Organometallics* **1994**, *13*, 2532. Copyright 1994 American Chemical Society.]

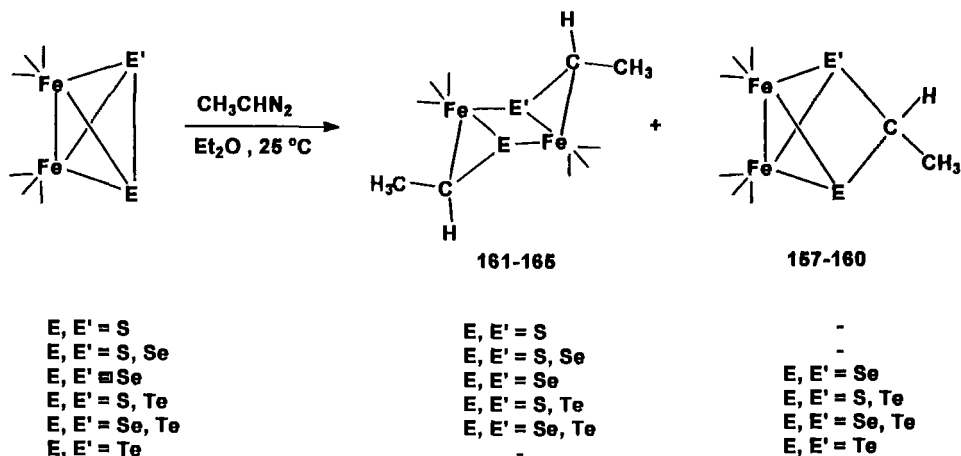
TABLE I
ENERGIES OF THE LUMO AND HOMO AND BINDING ENERGIES OF FOUR ISOMERS OF
[(CO)₆Fe₂STe{μ-C(H)=C(C≡CMe)}] (**156**) IN eV

	Isomers ^a			
	isomers ^a			
LUMO	-9.974	-9.828	-9.009	-9.645
HOMO	-10.274	-10.241	-9.975	-9.952
Binding energy	-148.686	-148.532	-142.767	-142.952

^a R = -C≡CMe; R' = -C≡CH.

which has been structurally characterized. The molecule consists of a Fe₂Te₂ butterfly geometry with both the methyl groups bonded to the two wing-tip Te atoms in equatorial positions. **169** reacts with diiodomethane to yield the compound **166**.

The reactions of the mixed-chalcogenide compounds **113** and **114** with diazomethane are more complex, with numerous products being formed.



SCHEME 9.

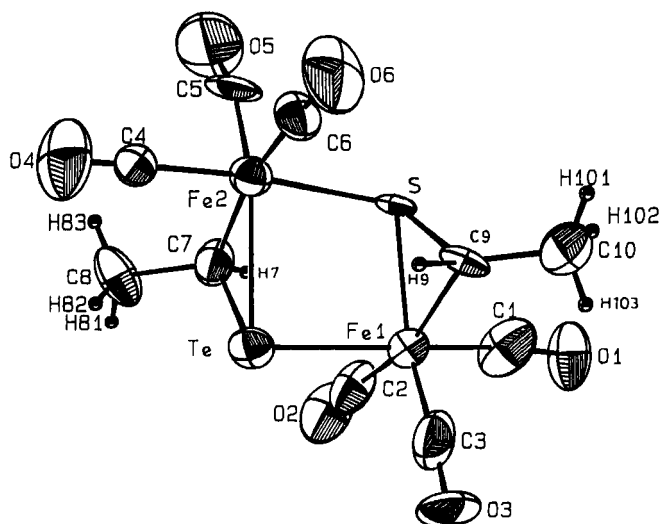


FIG. 53. Molecular structure of $(\text{CO})_6\text{Fe}_2\text{STe}\{\text{C}(\text{H})\text{CH}_3\}_2$ (**164**). [Reprinted with kind permission from Mathur, P.; Manimaran, B.; Satyanarayana, C. V. V.; Varghese, B. Synthesis, spectroscopic and structural characterisation of $(\text{CO})_6\text{Fe}_2\text{EE}'\{\text{C}(\text{H})\text{CH}_3\}_2$ and $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC}(\text{H})\text{CH}_3\text{E}'\}$, (E, E' = S, Se, Te). *J. Organomet. Chem.* **1997**, 527, 83. Copyright Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

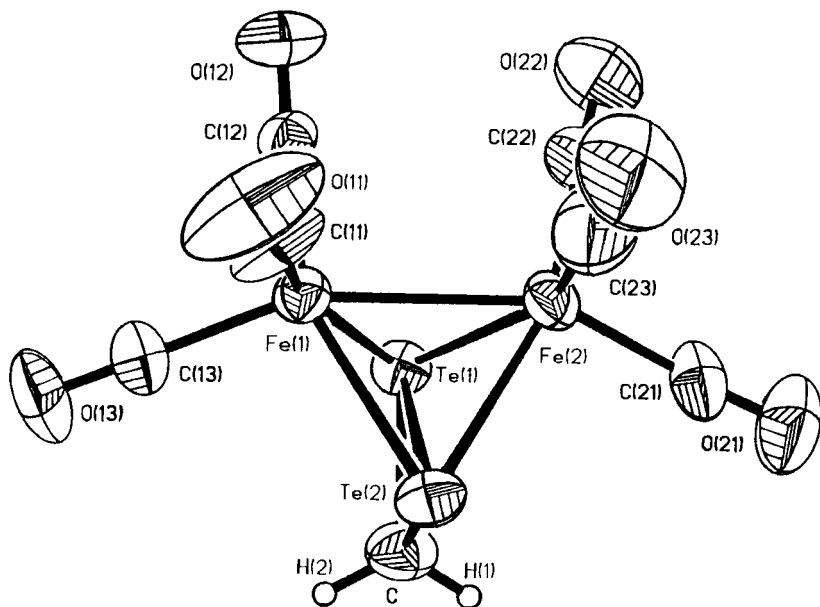


FIG. 54. Molecular structure of $(\text{CO})_6\text{Fe}_2(\mu\text{-TeCH}_2\text{Te})$ (**166**). [Reprinted with kind permission from Mathur, P.; Reddy, V. D.; Bohra, R. Addition of methylene groups to $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Te})_2$. *J. Organomet. Chem.* **1991**, 401, 339. Copyright 1991 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

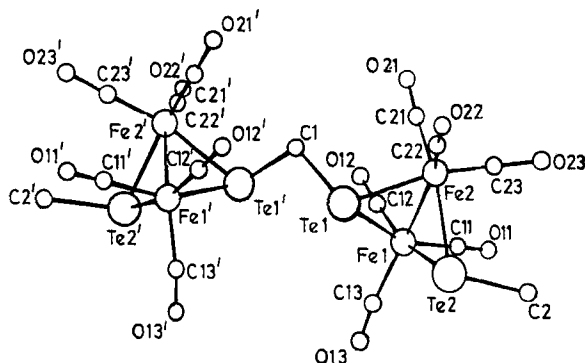


FIG. 55. Molecular structure of $[(\mu\text{-CH}_3\text{Te})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-Te}(\text{CH}_2)\text{Te-}\mu]$ (**167**). [Reprinted with kind permission from Mathur, P.; Reddy, V. D.; Das, K.; Sinha, U. C. Synthesis and structural characterisation of a new methylene bridged double butterfly shaped complex $[(\mu\text{-CH}_3\text{Te})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-Te}(\text{CH}_2)\text{Te-}\mu]$. *J. Organomet. Chem.* **1991**, 409, 255. Copyright 1991 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

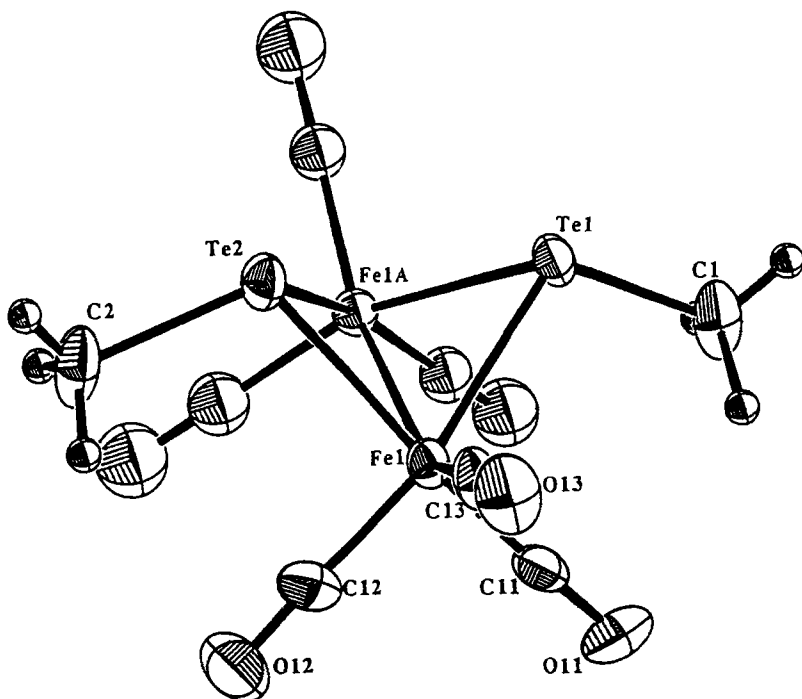


FIG. 56. Molecular structure of $(\text{CO})_6\text{Fe}_2(\mu\text{-TeMe})_2$ (**170**). [Reprinted with permission from Bachman, R. E.; Whitmire, K. H. *Organometallics* **1993**, 12, 1988. Copyright 1993 American Chemical Society.]

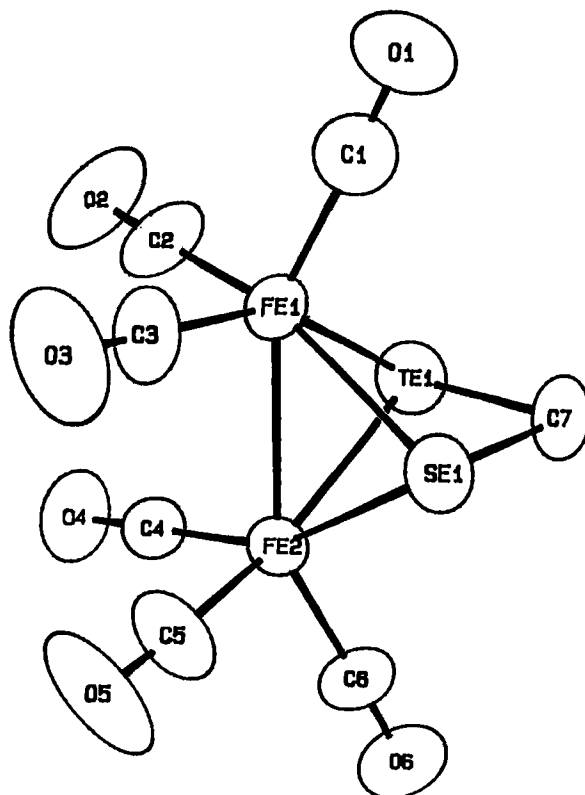


FIG. 57. Molecular structure of $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{Te})$ (**172**). [Reprinted with kind permission from Mathur, P.; Manimaran, B.; Hossain, M. M.; Shanbag, R.; Murthy, J.; Saranathan, I. S.; Satyanarayana, C. V. V.; Bhadbhade, M. M. Synthesis and characterisation of methylene-inserted mixed-chalcogenide compounds $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{Te})$ and $(\text{CO})_6\text{Fe}_2(\mu\text{-SCH}_2\text{Te})$. *J. Organomet. Chem.* **1995**, 490, 173. Copyright 1995 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

The major products in these reactions are $[(\text{CO})_6\text{Fe}_2(\mu\text{-SCH}_2\text{Te})]$ (**171**) and $[(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{Te})]$ (**172**) (Fig. 57), respectively.¹¹⁶

In the reaction of **113** with diazomethane, one of the minor products has been isolated and characterized as $[(\text{CO})_3\text{Fe}(\mu\text{-CH}_2\text{Te})_2]$ (**173**) (Fig. 58).¹¹⁷

The core geometry of **173** consists of a square in which Fe and Te atoms occupy alternate corners. Two Fe–Te bonds are bridged by a CH_2 group, one on each side of the plane defined by the heavy atoms, to give an overall chairlike structure. The formation of **173** is not observed in the reaction of **110** with diazomethane.

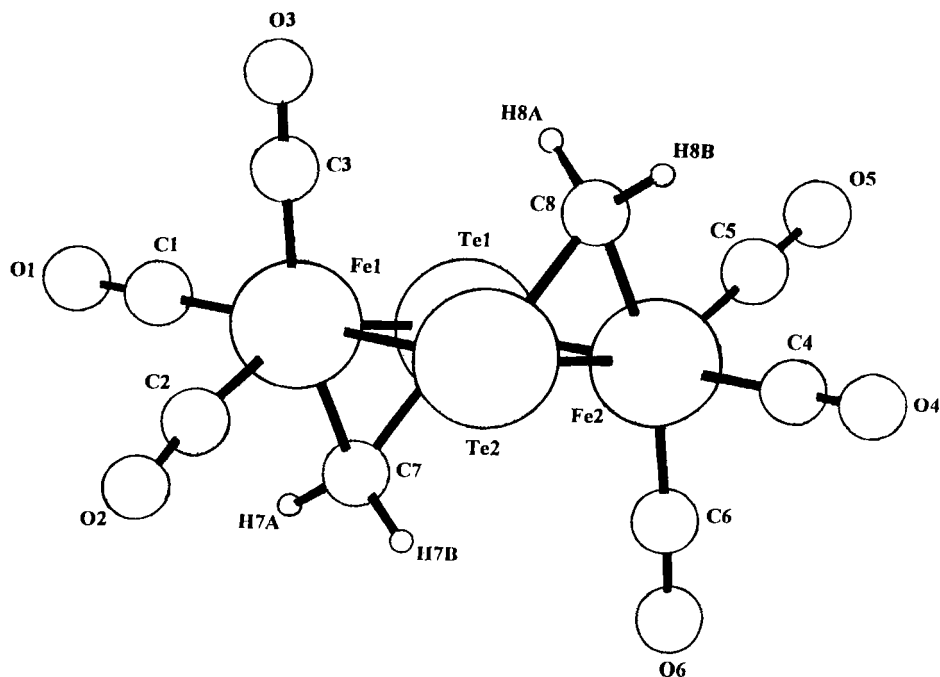


FIG. 58. Molecular structure of $[(\text{CO})_3\text{Fe}(\mu\text{-CH}_2\text{Te})_2]$ (**173**). [Reprinted with kind permission from Mathur, P.; Manimaran, B.; Hossain, M. M.; Satyanarayana, C. V. V.; Puranik, V. G.; Tavale, S. S. Insertion of methylene group into Fe–Te bond. Synthesis and characterisation of $[(\text{CO})_3\text{Fe}(\mu\text{-CH}_2\text{Te})_2]$. *J. Organomet. Chem.* **1995**, 493, 251. Copyright 1995 Elsevier Science S. A., P.O. Box 564, 1001 Lausanne, Switzerland.]

E. Mono-, Di-, and Tri-chalcogenide, Fe/Mo Clusters

The room-temperature reaction of **77** with $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ yields the clusters $\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_4\text{-Se})(\mu_3\text{-Se})_2$ (**174**) (Fig. 59) and $\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-Se})_2$ (**175**) (Fig. 60) (Scheme 10)¹¹⁸; there is no indication of any formation of the Se analogs of the *cis*-“Braunstein” (**176 A**) or *trans*-“Curtis” (**176 B**) isomers (Scheme 11).^{119,120}

It is shown that if an acetylenic moiety is added to **77**, the reactive Se sites are blocked and addition can take place at the Fe centers. For instance, thermolysis of **127** and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ yields a cluster **174** in which the Fe–Fe bond of $\text{Fe}_2(\text{CO})_6$ unit has been cleaved.¹²¹

When a benzene solution containing **80** and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ is refluxed, the major products formed are **175** and $\text{Cp}_2\text{Mo}_2\text{Fe}(\mu_3\text{-Se})(\text{CO})_7$ (**177**) (Fig. 61). A small amount of the trichalcogenide cluster **174** is also formed.

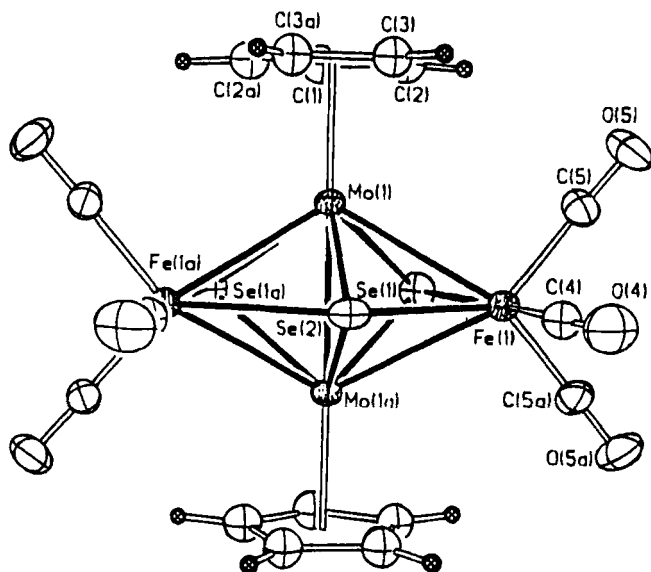


FIG. 59. Molecular structure of $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_4\text{-Se})(\mu_3\text{-Se})_2]$ (**174**). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Rheingold, A. L. *Organometallics* **1993**, *12*, 5029. Copyright 1993 American Chemical Society.]

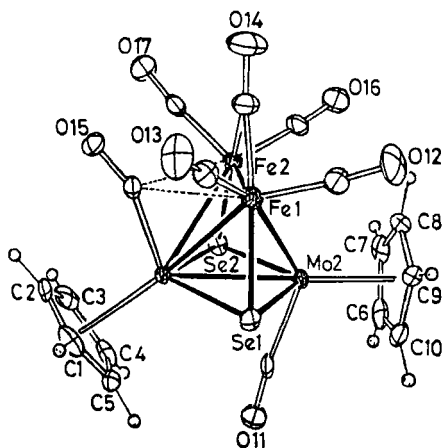
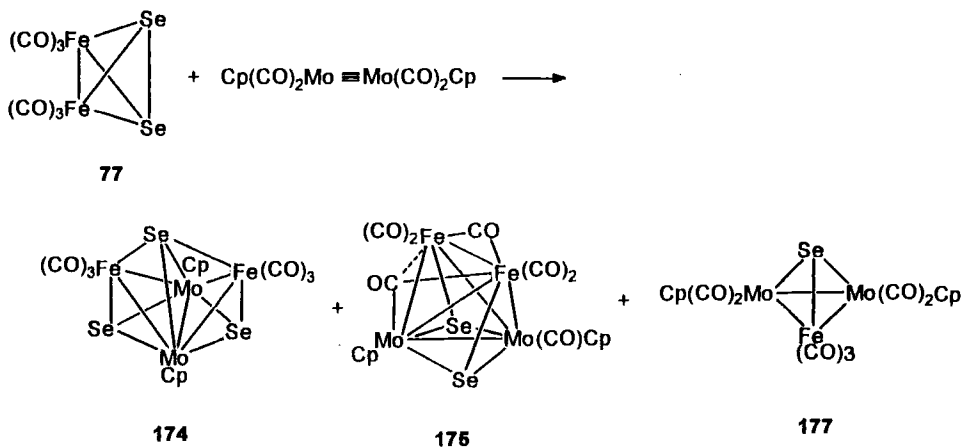
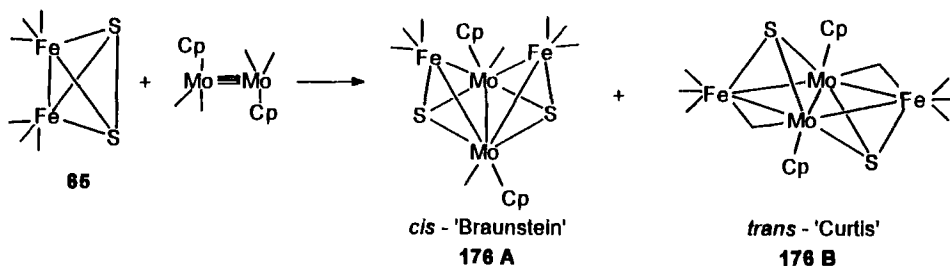


FIG. 60. Molecular structure of $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-Se})_2]$ (**175**). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Rheingold, A. L. *Organometallics* **1994**, *13*, 3909. Copyright 1994 American Chemical Society.]



SCHEME 10.

The formation of **175** from the room-temperature reaction of **77** and $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ is thought to occur by the addition of the Mo_2 compound across the Se–Se bond of **77**, accompanied by the loss of three CO groups. The formal loss of one CO group and scission of the Fe–Fe bond would result in the Braunstein/Curtis analog, $\text{Cp}_2\text{Mo}_2\text{Fe}_2\text{Se}_2(\text{CO})_8$ (**176 A** or **176 B**). Because this is not observed, it is possible that even if it is formed, it quickly undergoes a further loss of one CO group and reformation of the Fe–Fe bond to yield **175**. On thermolysis, **175** yields the trichalcogenide cluster **174**. This is thought to take place by a process involving scission of the Fe–Fe bond and addition of a Se atom to the open face of the Fe_2Mo_2 butterfly tetrahedron thus formed. Overall, there is also a loss of one CO group. The source of the third Se atom is thought to be the substantial decomposition of **175** in solution.



SCHEME 11.

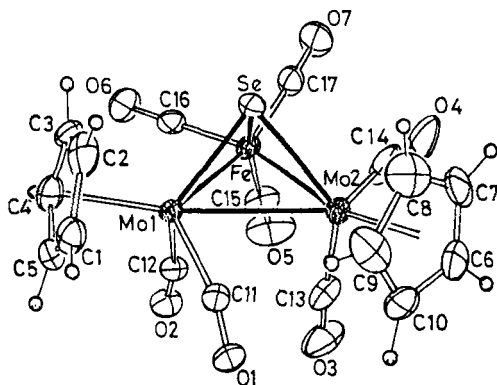


FIG. 61. Molecular structure of $[\text{Cp}_2\text{Mo}_2\text{Fe}(\text{CO})_7(\mu_3\text{-Se})]$ (**177**). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Rheingold, A. L. *Organometallics* **1994**, *13*, 3909. Copyright 1994 American Chemical Society.]

On thermolysis or photolysis, **80** is known to fragment to form **77** as well as $\text{Fe}(\text{CO})_x$ fragments. Therefore, the formation of **175** from the thermolytic reaction of **80** and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ probably occurs via an initial formation of **77** and addition of a Mo_2 unit to it. Also, the formation of **175** may be accounted for by the presence of $\text{Fe}(\text{CO})_x$ and Se fragments resulting from fragmentation of **180** on thermolysis. The Te analogs $\text{Cp}_2\text{Mo}_2\text{Fe}_2\text{Te}_3(\text{CO})_6$ (**178**), $\text{Cp}_2\text{Mo}_2\text{Fe}_2\text{Te}_2(\text{CO})_7$ (**179**), and $\text{Cp}_2\text{Mo}_2\text{FeTe}_2(\text{CO})_7$ (**180**) have been obtained from the high-temperature and high-CO-pressure reaction of **101** and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$.¹²² Thermolysis of **180** forms **178**, **179**, and $\text{Cp}_2\text{Mo}_2\text{FeTe}(\text{CO})_7$ (**181**) (Fig. 62).

The S-capped cluster, $\text{Cp}_2\text{Mo}_2\text{FeS}(\text{CO})_7$ (**182**), has been prepared from a metal-exchange reaction involving the replacement of two $\text{Co}(\text{CO})_3$ groups of $\text{FeCo}_2(\mu_3\text{-S})(\text{CO})_9$ (**183**) with two $\text{CpMo}(\text{CO})_2$ units.¹²³ The S- or Se-arachno clusters, $\text{Cp}_2\text{Mo}_2\text{FeS}_2(\text{CO})_7$ or $\text{Cp}_2\text{Mo}_2\text{FeSe}_2(\text{CO})_7$, have not been observed.

When benzene solutions containing the mixed-chalcogenide $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})(\mu_3\text{-E}')]]$ ($\text{E}, \text{E}' = \text{S}, \text{Te}$ (**184**), Se, Te (**185**)) and $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ are refluxed, three different classes of mixed Fe/Mo mixed-metal clusters are obtained in each case: those containing one bridging chalcogen ligand, S (**182**), Se (**177**), or Te (**181**); those containing two chalcogen ligands, STe (**186**), SeSe (**175**), SeTe (**187**), or TeTe (**179**); and those with three chalcogen ligands, S_2Te (**188**), STe_2 (**189**), Se_3 (**174**), Se_2Te (**190**), Te_2Se (**191**), or Te_3 (**178**)) (Table II). In the thermolytic reaction between $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})(\mu_3\text{-Se})]$ (**192**) and $[\text{Cp}_2\text{Mo}_2(\text{CO})_6]$, the monochalcogenide compounds **182** or **177** are not observed; however, the di-SSe (**193**) and SeSe (**175**) and tri- S_2Se (**194**), SSe_2 (**195**), and Se_3 (**174**) chalcogenide clusters are formed.^{124,125}

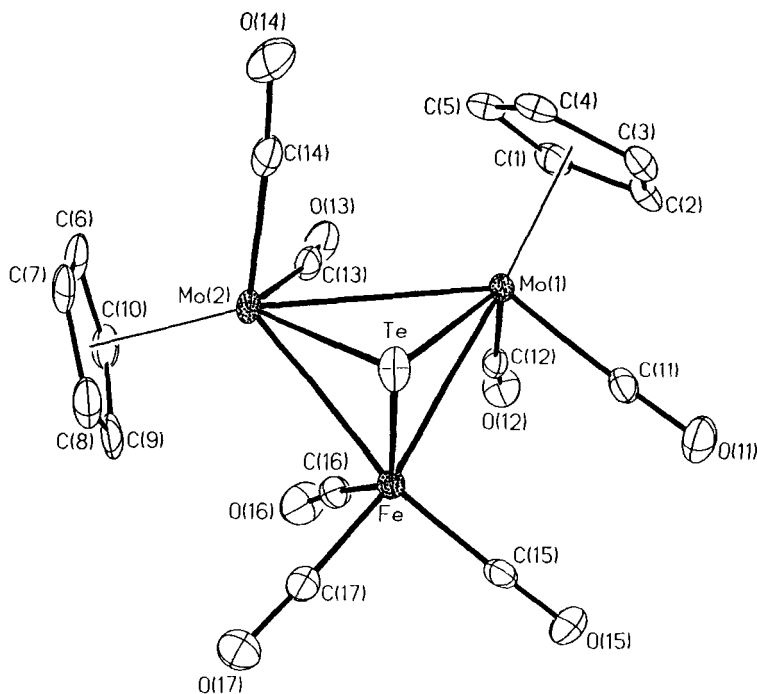


FIG. 62. Molecular structure of $[\text{Cp}_2\text{Mo}_2\text{Fe}(\text{CO})_7(\mu_3\text{-Te})]$ (**181**). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Umbarkar, S. B.; Satyanarayana, C. V. V.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. *Organometallics* **1996**, *15*, 1898. Copyright 1996 American Chemical Society.]

The dichalcogenide clusters can be converted to the trichalcogenide clusters, in good yields, on refluxing in benzene solvent with chalcogen powder (Scheme 12).

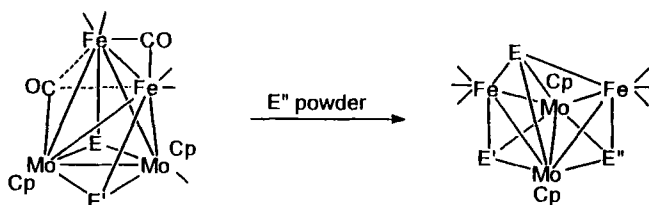
The formation of the trichalcogenide clusters from the thermolysis of chalcogens with $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-E})(\mu_3\text{-E}')]]$ formally involves the cleavage of the Fe–Fe bond and loss of one CO group of $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-E})(\mu_3\text{-E}')]]$. Formation of $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_4\text{-Te})(\mu_3\text{-Se})(\mu_3\text{-S})]$ (**196**) (Fig. 63) provides an example of a mixed-metal cluster containing all three different types of chalcogen ligand.¹²⁴ The larger chalcogen atom is seen to occupy the μ_4 -bonding site.

Thus, in thermolysis reactions involving $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-E})(\mu_3\text{-Te})]$ with S or Se, there must be a shift of the Mo_2Fe -face-capping $\mu_3\text{-Te}$ to the μ_4 -coordination seen in the trichalcogenide, and the incoming chalcogen atom μ_3 -caps one Mo_2Fe face.

The trichalcogenide clusters are isostructural, the basic geometry consisting of two FeMo_2 triangular arrays with a common Mo_2 edge. Each

TABLE II
FORMATION OF MONO-, DI-, AND TRICHALCOGENIDE MIXED Fe/Mo CLUSTERS

Reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ with:	Products		
	Monochalcogenides $\text{Cp}_2\text{Mo}_2\text{Fe}(\text{CO})_7(\mu_3\text{-E})$	Dichalcogenides $\text{Cp}_2\text{Mo}_2\text{Fe}(\text{CO})_7(\mu_3\text{-E})(\mu_3\text{-E}')$	Trichalcogenides $\text{Cp}_2\text{Mo}_2\text{Fe}(\text{CO})_7(\mu_4\text{-E})(\mu_3\text{-E}')(\mu_3\text{-E}'')$
$\text{Fe}_3\text{STe}(\text{CO})_9$ (184)	E = S (182)	E = E' = Te (179)	E = E' = E'' = Te (178)
	E = Te (181)	E = S, E' = Te (186)	E = Te, E' = E'' = S (188)
$\text{Fe}_3\text{SeTe}(\text{CO})_9$ (185)	E = Se (177) E = Te (181)	E = E' = Te (179)	E = E' = Te, E'' = S (189)
		E = E' = Se (175)	E = E' = E'' = Te (178)
		E = Se, E' = Te (187)	E = E' = E'' = Se (174)
		E = E' = Te (179)	E = Te, E' = E'' = Se (190)
$\text{Fe}_3\text{SSe}(\text{CO})_9$ (192)		E = E' = Te, E'' = Se (191)	E = E' = Te, E'' = Se (191)
		E = E' = Se (177)	E = E' = E'' = Se (174)
		E = S, E' = Se (193)	E = E' = Se, E'' = S (195)
			E = Se, E' = E'' = S (194)



SCHEME 12.

FeMo_2 plane has a μ_3 -bonded chalcogen atom above it, and in addition there is a third chalcogen atom that is μ_4 -bonded to all four metal atoms. The Mo–Mo bond distance increases with the size of the μ_3 -chalcogen atom (Table III).

The dichalcogenide clusters are isostructural, and the basic cluster geometry of these consists of a Fe_2Mo_2 tetrahedron with the two Mo_2Fe faces capped by μ_3 -chalcogen atoms. In all of these, one of the Mo atoms possesses

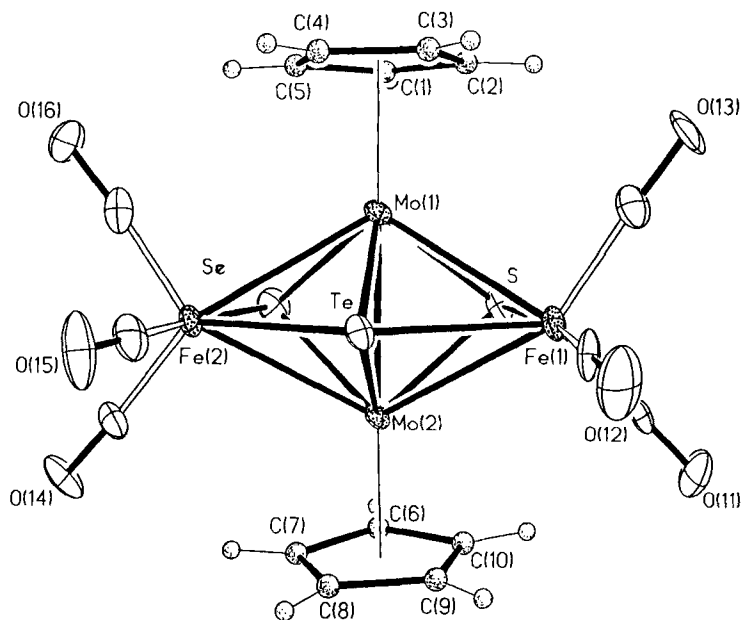


FIG. 63. Molecular structure of $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_4\text{-Te})(\mu_3\text{-Se})(\mu_3\text{-S})]$ (196). [Reprinted with permission from Mathur, P.; Hossain, M. M.; Umbarkar, S. B.; Satyanarayana, C. V. V.; Rheingold, A. L.; Liabe-Sands, L. M.; Yap, G. P. A. *Organometallics* **1996**, 15, 1898. Copyright 1996 American Chemical Society.]

TABLE III
VARIATION OF MO—MO BOND DISTANCE IN $\text{Cp}_2\text{Mo}_3\text{Fe}_2(\mu_4\text{-E})(\mu_3\text{-E}')(\mu_3\text{-E}'')$ CLUSTERS

Mo—Mo bond length (Å) for $\text{Cp}_2\text{Mo}_2\text{Fe}_2(\mu_4\text{-E})(\mu_3\text{-E}')(\mu_3\text{-E}'')$	E	E'	E''
2.8172(12)	Te	Te	Te
2.7510(13)	Te	Te	S
2.743(2)	Se	Se	Se
2.739(2)	Te	Se	S
2.725(2)	Te	S	S

a semitriply bridging CO ligand. Each Fe atom has two terminally bonded carbonyl groups, and one CO ligand bridges the Fe—Fe bond. The structure of the monochalcogenide clusters is a tetrahedron composed of two Mo, one Fe, and one chalcogen atoms. Each Mo atom possesses one Cp and two CO groups, and the Fe atom has three CO groups bonded to it.^{124,125}

F. Addition of Metal Fragments to $\text{Fe}_2\text{E}_2(\text{CO})_6$

Metal-containing groups can be inserted into the chalcogen—chalcogen bond of $[\text{Fe}_2(\text{CO})_2(\text{E}_2)]$ under facile conditions. The insertion of metal-containing groups can occur such that mixed-metal complexes of the structure shown in Fig. 64 are formed (Table IV).

Insertion of coordinatively unsaturated species into the chalcogen—chalcogen bonds can also be accompanied by formation of new metal—metal bonds, giving rise to square-pyramidal cluster cores (Fig. 65). These can be of two types, one in which the hetero-metal atom occupies an apical site (A) and another in which the hetero-metal atom is located on the basal site (B).

The cluster $[\text{CpRhFe}_2(\text{CO})_6(\mu_3\text{-Te})_2]$ (**213**) exists in solution as an equilibrating mixture of two isomers, one in which the rhodium atom is in a basal site of the Fe_2RhTe_2 square pyramid, and another in which it occupies the apical site.¹³¹ In several other mixed-metal clusters that also exhibit a

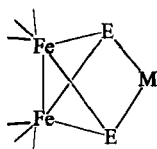


FIG. 64. Structure of $\text{Fe}_2\text{E}_2\text{M}$.

TABLE IV
COMPOUNDS OF THE FORM $[(\text{CO})_6\text{Fe}_2(\mu_3\text{-E})(\mu_3\text{-E}')\text{M}]$ (Fig. 64)

E, E'	M	Ref.
Te, Te	$\text{Fe}(\text{CO})_3(\text{PPh}_3)$ (197)	126
	$\text{M}(\text{PPh}_3)_2$	
	M = Ni (198), Pd (199), Pt (200)	127
	Cp_2Ti (201)	128
Se, Te	SnR_2 (R = Me (202), <i>n</i> -Bu (203))	128
	$\text{Pt}(\text{PPh}_3)_2$ (204)	129
	$\text{Fe}(\text{CO})_3(\text{PPh}_3)$ (205)	129
S, Te	$\text{M}(\text{PPh}_3)_2$	
	M = Pd (206), Pt (207)	86
	$\text{Fe}(\text{CO})_3(\text{PPh}_3)$ (208)	86
Se, Se	$\text{M}(\text{PPh}_3)_2$	
	M = Pd (209), Pt (210)	130
S, S	$\text{M}(\text{PPh}_3)_2$	
	M = Pd (211), Pt (212)	130

square-pyramidal core, the heterometal atom is found only in the apical site (Table V). For instance, at room temperature, the compounds $[\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')]$ react with $[\text{M}(\text{CO})_5(\text{THF})]$ (M = Mo, W) to form $[\text{Fe}_2\text{M}(\text{CO})_{10}(\mu_3\text{-E})(\mu_3\text{-E}')]$ (Fig. 66).

If an excess of $[\text{Mo}(\text{CO})_5(\text{THF})]$ is made to react with **114**, the mixed-metal cluster $[\text{Fe}_4\text{Mo}(\text{CO})_{14}(\mu_3\text{-Se})_2(\mu_3\text{-Te})_2]$ (**222**) (Fig. 67) (Scheme 13), with an unusual “hourglass” cluster core shape, is formed.¹³⁶

In **222**, the Mo atom occupies the common apical site of two distorted square-pyramidal cores, in each of which the two Fe atoms, one Se atom, and one Te atom occupy the basal sites. The formation of **222** demonstrates the contrast in the influence of the chalcogens in cluster-expansion reactions. Although **77** readily reacts with $[\text{M}(\text{CO})_5(\text{THF})]$ (M = W, Mo) to form $[\text{Fe}_2\text{M}(\text{CO})_{10}(\mu_3\text{-Se})_2]$ (M = W (**217**), Mo (**218**)), **110** reacts with the tungsten compound only to form **216**; formation of $[\text{Fe}_2\text{Mo}(\text{CO})_{10}(\mu_3\text{-Te})_2]$ is not observed. An intermediate situation arises when the mixed-chalcogenide compound **114** is used for reacting with $[\text{Mo}(\text{CO})_5(\text{THF})]$. The formation

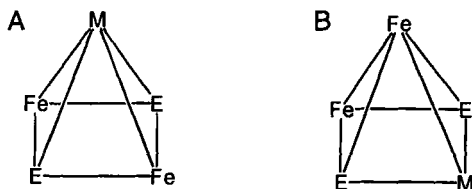


FIG. 65. Square-pyramidal structures of $\text{Fe}_2\text{E}_2\text{M}$.

TABLE V
CLUSTERS OF FORM $[\text{Fe}_2\text{M}(\text{CO})_{10}(\mu_3\text{-E})(\mu_3\text{-E}')]$

E, E'	M	Ref.
S, Te	W (214), Mo (215)	132
Te, Te	W (216)	133
Se, Se	W (217)	133, 134
Se, Se	W (218)	133, 134
Se, Te	W (219)	134
S, Se	W (220)	134
S, S	W (221)	135

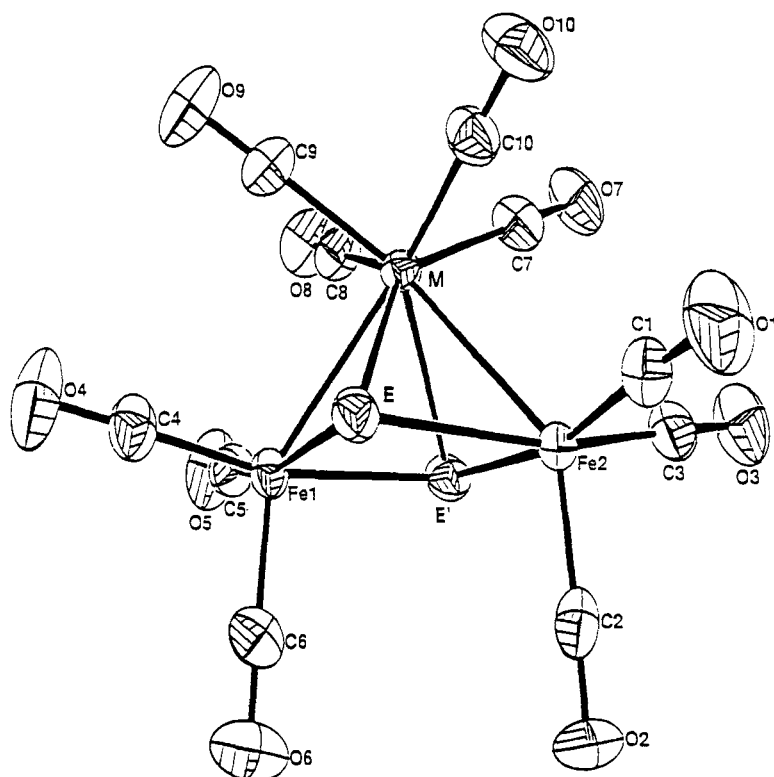


FIG. 66. Molecular structure of $[\text{Fe}_2\text{M}(\text{CO})_{10}(\mu_3\text{-E})(\mu_3\text{-E}')]$, M = W, E = Se, E' = Se, Te; M = Mo, E = E' = Se. [Reprinted with permission from Mathur, P.; Sekar, P.; Satyanarayana, C. V. V.; Mahon, M. F. *J. Chem. Soc., Dalton. Trans.* **1996**, 2173. Copyright 1996 Royal Society of Chemistry.]

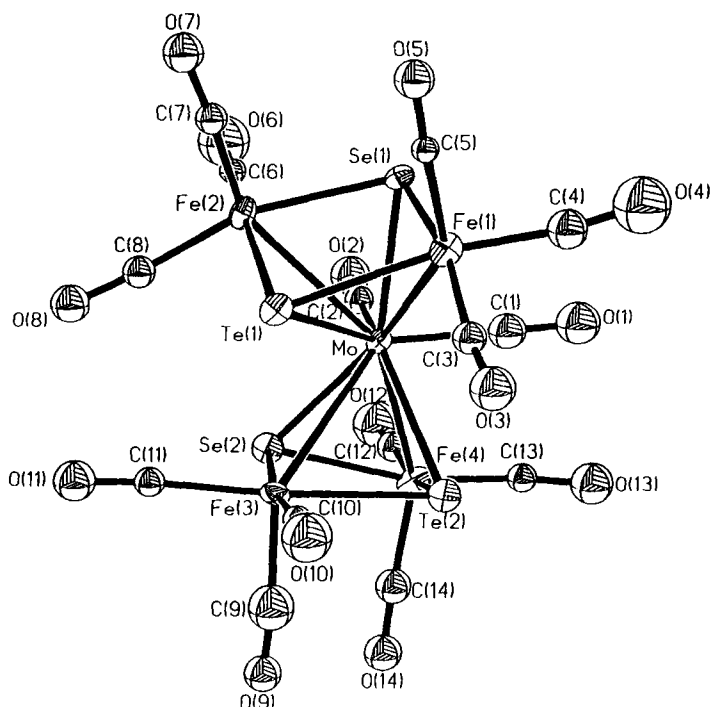
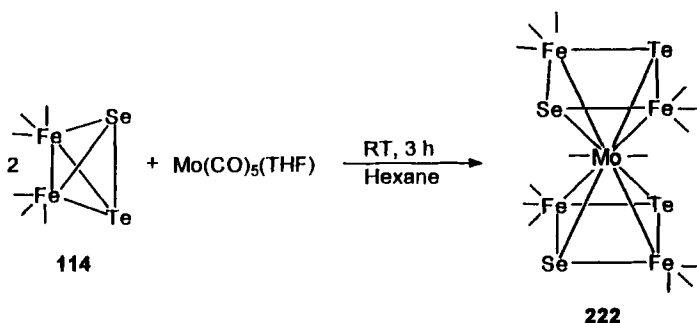


FIG. 67. Molecular structure of $[\text{Fe}_4\text{Mo}(\text{CO})_{14}(\mu_3\text{-Se})_2(\mu_3\text{-Te})_2]$ (**222**). [Reprinted with permission from Mathur, P.; Sekar, P. *J. Chem. Soc., Chem. Commun.* **1996**, 727. Copyright 1996 Royal Society of Chemistry.]

of $[\text{Fe}_2\text{Mo}(\text{CO})_{10}(\mu_3\text{-Se})(\mu_3\text{-Te})]$ (**223**) is observed; however, it quickly converts to **222**.

Attempts to add $[\text{Fe}_2(\text{CO})_6\text{E}_2]$ groups to the homochalcogenide compounds $[\text{Fe}_2\text{M}(\text{CO})_{10}(\mu_3\text{-E})_2]$ ($\text{E} = \text{Se}, \text{Te}$) have been unsuccessful.



SCHEME 13.

TABLE VI
CLUSTERS OF FORM $\text{Fe}_2\text{M}(\text{CO})_6\text{EE}'$ ($\text{M} = \text{CpCo}$ or Cp^*Co)

E, E'	M	Ref.
Se, Se	CpCo (224) (Fig. 68)	137, 138
S, Se	CpCo (225) (Fig. 69)	138
S, S	Cp^*Co (226) ^a	63
S, Te	CpCo (227)	139
Se, Te	CpCo (228)	139

^a $\text{Cp}^* = \text{C}_5\text{Me}_5$.

The fragment CpCo has also been added to the chalcogen atoms of $[\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)]$ compounds. Structure determinations of some of these reveal that the insertion of the Co species into the E-E bond is accompanied

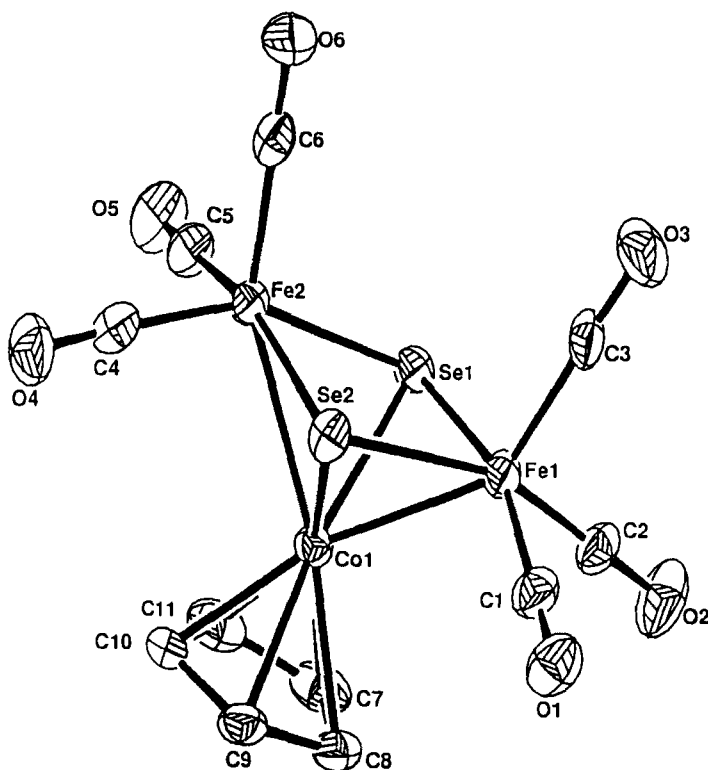


FIG. 68. Molecular structure of $[\text{CoCpFe}_2(\text{CO})_6(\mu_3\text{-Se})_2]$ (**224**). [Reprinted with permission from Mathur, P.; Sekar, P.; Satyanarayana, C. V. V.; Mahon, M. F. *Organometallics* **1995**, *14*, 2115. Copyright 1995 American Chemical Society.]

by two new Fe–Co bond formations, and the Co is situated at the apical site of the square-pyramidal core (Table VI, Figs. 68 and 69).

G. Antiferromagnetic Clusters

The binuclear antiferromagnetic complex $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)_2(\mu\text{-S})]$ (**229**) can act as an initial metal-containing ligand toward a variety of unsaturated metal fragments ML_n following cluster “block-building” sequences (Scheme 14).^{140,141}

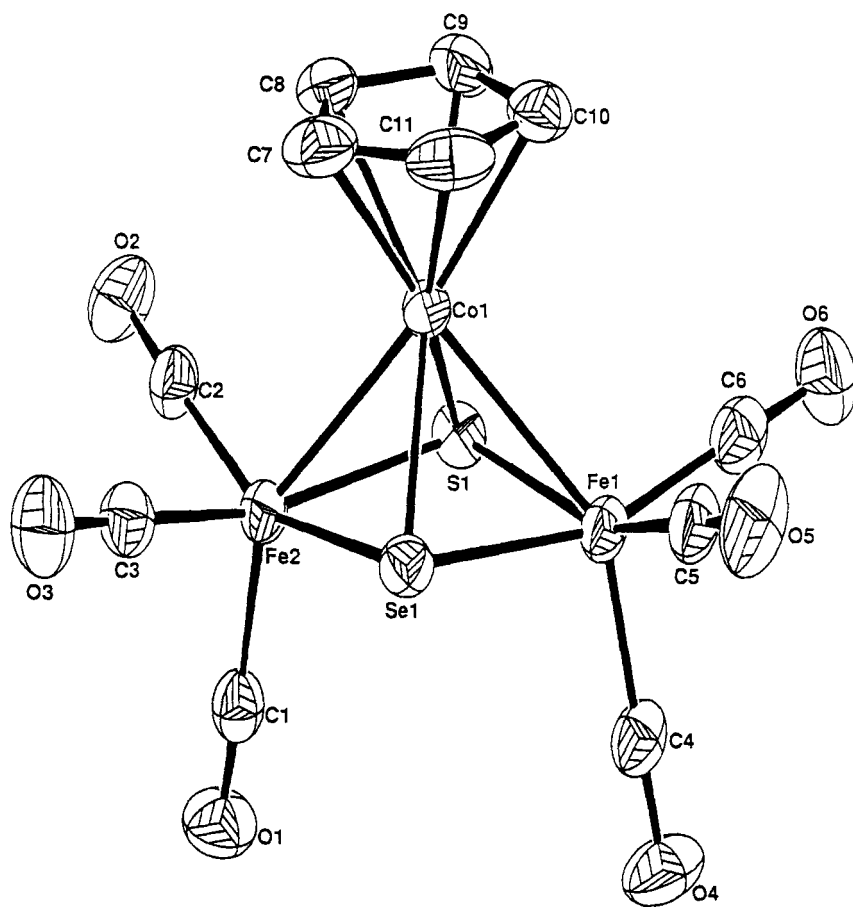
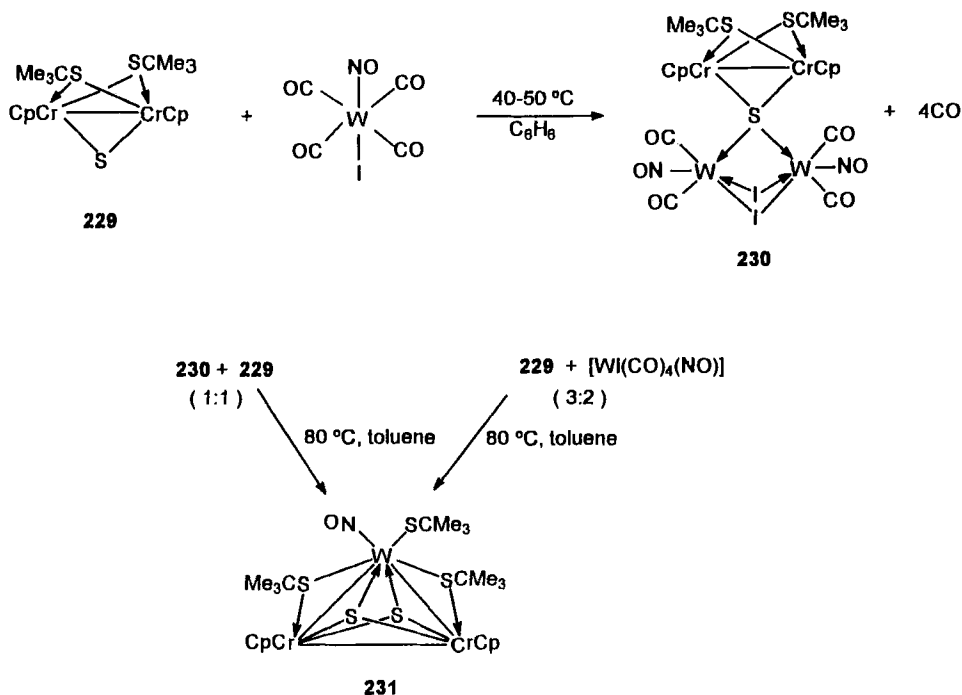


FIG. 69. Molecular structure of $[\text{CoCpFe}_2(\text{CO})_6(\mu\text{-SSe})]$ (**225**). [Reprinted with permission from Mathur, P.; Sekar, P.; Satyanarayana, C. V. V.; Mahon, M. F. *Organometallics* **1995**, *14*, 2115. Copyright 1995 American Chemical Society.]

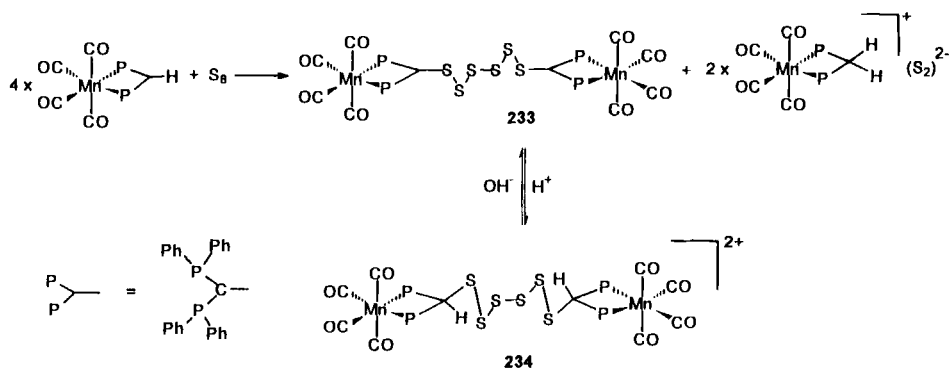


SCHEME 14.

The reaction between **229** and $[\text{W}(\text{CO})_4(\text{NO})]$ at $40\text{--}50^\circ\text{C}$ forms predominantly the antiferromagnetic adduct $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)_2(\mu_4\text{-S})\text{W}_2(\mu\text{-I})_2(\text{CO})_4(\text{NO})_2]$ (**230**). Further heating of **230** in the presence of an excess of **229** affords the trinuclear antiferromagnetic cluster $[\text{Cp}_2\text{Cr}_2(\mu_3\text{-S})_2(\mu\text{-SCMe}_3)_2\text{W}(\text{SCMe}_3)(\text{NO})]$ (**231**), which can also be prepared by direct reaction between **229** and $[\text{W}(\text{CO})_4(\text{NO})]$ at 80°C in toluene. This occurs via the formation of an unstable intermediate $[\text{CpCr}(\mu\text{-SCMe}_3)_2(\mu\text{-S})\text{W}(\text{CO})_2(\text{NO})]$ (**232**).

H. Sulfurization Reactions

A process of sulfurization of coordinated bis(diphenylphosphino)methanamide has provided access to the class of hexasulfur-bridged tetraphosphine and tetraphosphinobis(methanide)ligands. Treatment of a solution of $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}\}]$ with sulfur at room temperature forms a hexasulfur-bridged complex, $[(\text{CO})_4\text{Mn}\{(\text{PPh}_2)_2\text{C-S}_6\text{-C}(\text{PPh}_2)_2\}\text{Mn}(\text{CO})_4]$ (**233**) (Scheme 15).¹⁴²



SCHEME 15.

The formation of this complex is suggested to occur by an initial formation of the intermediate $[(\text{CO})_4\text{Mn}\{(\text{PPh}_2)_2\text{C}(\text{H})\text{S}_6\text{C}(\text{H})(\text{PPh}_2)_2\}\text{Mn}(\text{CO})_4]^+(\text{S}_2)^{2-}$ (**234**), arising from a nucleophilic degradation of S_8 . In support of this mechanism is the formation of **234** by protonation of **233** using HBF_4 . This process can be reversed by treatment of **234** with KOH . The structure of **233** has been established by X-ray methods (Fig. 70).

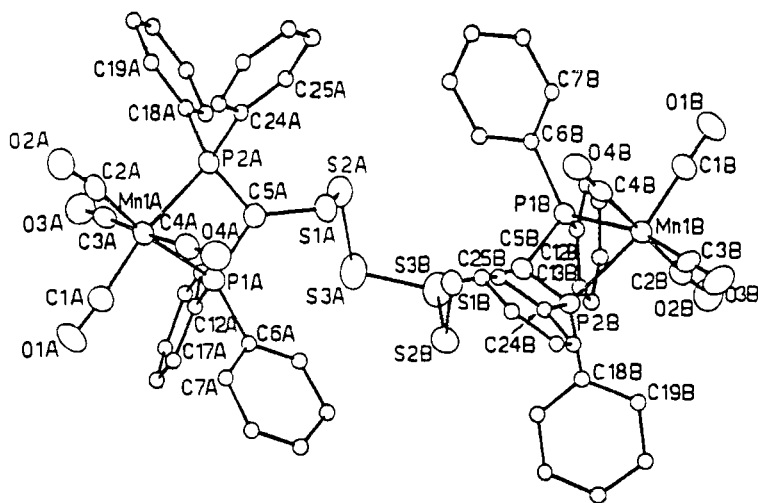


FIG. 70. Molecular structure of $[(\text{CO})_4\text{Mn}\{(\text{PPh}_2)_2\text{C}-\text{S}_6-\text{C}(\text{PPh}_2)_2\}\text{Mn}(\text{CO})_4]$ (**233**). [Reprinted with permission from Ruiz, J.; Riera, V.; Vivanco, M.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1996**, *15*, 1082. Copyright 1996 American Chemical Society.]

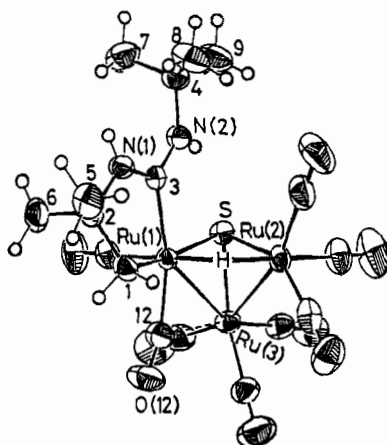


FIG. 71. Molecular structure of $[(\mu\text{-H})\text{Ru}_3(\text{CO})_8(\mu_3\text{-S})(\eta^2\text{-CH}_2\text{CMe}_2\text{NHCNH-}t\text{-Bu})]$ (**235**). [Reprinted with permission from Bodensieck, U.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Chem. Soc., Chem. Commun.* **1990**, 267. Copyright 1990 Royal Society of Chemistry.]

The thiourea derivative $(\text{Me}_3\text{CNH})_2\text{CS}$ reacts with $\text{Ru}_3(\text{CO})_{12}$ with $\text{C}=\text{S}$ bond cleavage and oxidative addition of the nonactivated C-H bond of a peripheral methyl group to form $\mu_3\text{-S}$ and $\mu_4\text{-S}$ bridged clusters, $[(\mu\text{-H})\text{Ru}_3(\text{CO})_8(\mu_3\text{-S})(\eta^2\text{-CH}_2\text{CMe}_2\text{NHCNH-}t\text{-Bu})]$ (**235**) (Fig. 71) and $[(\mu\text{-H})\text{Ru}_3(\text{CO})_9\{\mu_3\text{-S-Ru}(\text{CO})_3(\mu_2\text{-CH}_2\text{CMe}_2\text{NHCNH-}t\text{-Bu})\}]$ (**236**) (Fig. 72).¹⁴³ In this reaction the thiourea is formally cleaved into a sulfur fragment and a diaminocarbene fragment, which are both coordinated to ruthenium.

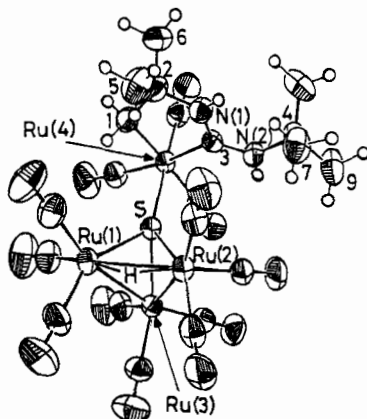


FIG. 72. Molecular structure of $[(\mu\text{-H})\text{Ru}_3(\text{CO})_9\{\mu_3\text{-S-Ru}(\text{CO})_3(\mu_2\text{-CH}_2\text{CMe}_2\text{NHCNH-}t\text{-Bu})\}]$ (**236**). [Reprinted with permission from Bodensieck, U.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Chem. Soc., Chem. Commun.* **1990**, 267. Copyright 1990 Royal Society of Chemistry.]

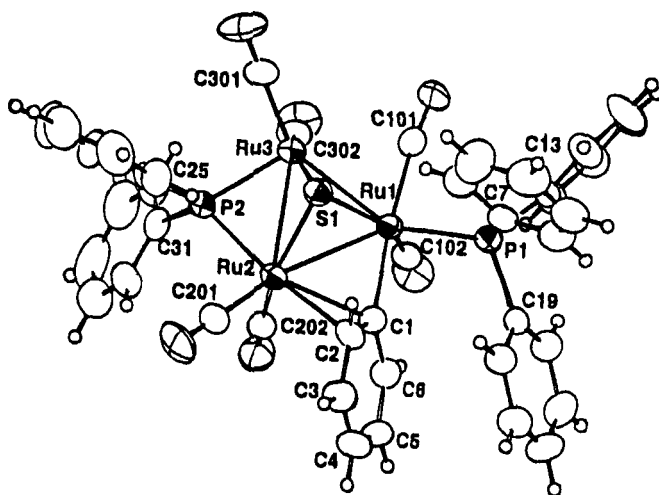


FIG. 73. Molecular structure of $[\text{Ru}_3(\text{CO})_7(\mu_2\text{-Ph})(\mu_2\text{-PPh}_2)(\text{PPh}_3)(\mu_3\text{-S})]$ (**238**). [Reprinted with permission from Hoferkamp, L.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *Organometallics* **1996**, *15*, 704. Copyright 1996 American Chemical Society.]

When a toluene solution of $[(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3, \eta^2\text{-SCNHPhNPh})]$ (**237**) is refluxed in presence of two equivalents of PPh_3 , the S-capped cluster $[\text{Ru}_3(\text{CO})_7(\mu_2\text{-Ph})(\mu_2\text{-PPh}_2)(\text{PPh}_3)(\mu_3\text{-S})]$ (**238**) (Fig. 73) is obtained.¹⁴⁴ The molecular structure of **238** shows the original trinuclear Ru framework where the only part of the diphenylthioureato ligand that remains is a capping $\mu_3\text{-S}$. A diphenylphosphido group bridges one Ru–Ru bond, and there is a phenyl bridge resulting from P–C bond activation of a PPh_3 group and C–H activation of the aryl group.

Thermolysis reaction of **237** forms two hexanuclear thioureato clusters, each with a metal skeleton that mimics a known conformer of cyclohexane: one that is similar to the boat conformer, $[\text{Ru}_6(\mu\text{-CO})(\text{CO})_{14}(\mu_4\text{-S})(\mu_4, \eta^2\text{-NPhCNHPh})(\mu_3, \eta^2\text{-SCNHPhNPh})]$ (**239**), and a second that is similar to the sofa conformer, $[(\mu\text{-H})_2\text{Ru}_6(\text{CO})_{16}(\mu_5\text{-S})(\mu_3, \eta^2\text{-SCNHPhNPh})]$ (**240**).¹⁴⁵ Cluster **240** is obtainable in reasonable yields, and its reactions with several donor ligands, PPh_3 , Me_2S , $\text{P}(n\text{-Bu})_3$, $\text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, and $t\text{-BuNC}$, have been investigated. These studies indicate that replacement of CO with certain isoelectronic ligands results in metal–metal bond-length changes relatively far removed from the substitution site. For instance, reaction of **240** with PPh_3 results in formation of $[(\mu\text{-H})\text{Ru}_6(\text{CO})_{15}(\text{PPh}_3)(\mu_5\text{-S})(\mu_3, \eta^2\text{-SCNHPhNPh})]$ (**241**), in which there is cleavage of one Ru–Ru bond and the original sofa-like structure of **240** has been somewhat distorted. Reaction with the other donor ligands results in

the substitution of a carbonyl group to give $[(\mu\text{-H})\text{Ru}_6(\text{CO})_{15}(\text{L})(\mu\text{-S})(\mu_3\text{-}, \eta^2\text{-SCNHPPhNPh})]$ ($\text{L} = \text{Me}_2\text{S}$ (**242**), $(n\text{-Bu})_3\text{P}$ (**243**), $\text{P}(\text{OMe})_3$ (**244**), $\text{P}(\text{OPh})_3$ (**245**), $t\text{-BuNC}$ (**246**)). The structures of these differ from that of **241** in that the substituting ligand occupies an axial site on the apical ruthenium atom at the end of the cluster opposite to that found in **241**.

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ISBN 0-12-031141-0



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